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# BIODEGRADATION AND SORPTION OF ORGANIC SOLVENTS AND HYDROCARBON FUEL CONSTITUENTS IN SUBSURFACE ENVIRONMENTS

J.T. WILSON, J.M. HENSON, M.D. PIWONI, B.H. WILSON,  
P. BANERJEE

U.S. EPA, RSKERL  
P.O. BOX 1198  
ADA, OKLAHOMA 74820

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hydrophobicity to a greater extent than predicted by hydrophobic sorption theory, probably because of interactions of the pollutants with mineral surfaces of the sorbents. However, no significant correlations between sorption and sorbent properties characteristic of mineral content were observed, indicating that site-specific sorption determinations will probably be necessary in developing optimized ground water reclamation strategies.

## SUMMARY

This report describes research pertaining to the biodegradation and sorption of chlorinated hydrocarbon solvents and hydrocarbon fuel constituents in subsurface environments. The primary goal of these studies was to provide necessary information to develop optimal strategies for decontamination of polluted ground water.

The degradation of chlorinated aliphatic hydrocarbons by subsurface microorganisms was examined. Soil microbial communities growing on light aliphatic hydrocarbons were found to be capable of co-metabolically degrading trichloroethylene and related compounds normally recalcitrant to biodegradation in aerobic subsurface environments. This microbial process has high potential as a basis for methodologies for removal of chlorinated hydrocarbon solvents from polluted ground water, both in-situ and in surface-based systems. Studies employing laboratory-scale fixed film bioreactors further illustrated the potential utility of the process in surface treatment systems and provided information needed for pilot-scale evaluation of such systems.

The possibility that light aromatic hydrocarbons might have a biological fate in anaerobic subsurface environments was also investigated. Benzene and several of its alkyl derivatives, all of which have been considered to be recalcitrant to biodegradation under anaerobic conditions, were observed to undergo relatively rapid and extensive biodegradation in anoxic aquifer materials. The anaerobic biodegradation of these relatively water-soluble aromatic constituents of distilled petroleum products has significant implications for the development of optimal strategies for remediation of ground water contaminated by hydrocarbon fuels.

Sorption data were developed for seven organic compounds of moderate hydrophobicity on subsurface solids obtained from various depths and containing varying quantities of native organic carbon. For low-carbon aquifer materials containing less than 0.2 percent native organic carbon, the sorbent compounds appeared to be sorbed to a greater extent than could be explained by hydrophobic partitioning to the solid phase carbon. Although interactions of the organic compounds with mineral surfaces of the aquifer solids were probably involved, no significant correlations could be discerned between sorption and those properties of the sorbents that were characteristic of their mineral components, such as clay content and surface area. This indicates that the development of optimal strategies for decontamination of polluted ground water will probably require site-specific sorption determinations using the relevant aquifer material and pollutants, at least until the variables governing pollutant sorption by low-carbon aquifer solids are better defined.

## PREFACE

This report was prepared by the Robert S. Kerr Environmental Research Laboratory (RSKERL), U.S. Environmental Protection Agency (U.S. EPA), Ada, OK 74820, under an Interagency Agreement between RSKERL and the Air Force Engineering and Services Center, Engineering and Services Laboratory, (HQ AFESC/RDVW), Tyndall Air Force Base, FL 32403-6001. The project was initiated by Captain Glen Tapio. The Air Force project officers were Captain Jack Jeter and Captain Richard A. Ashworth; Dr William J. Dunlap was the U.S. EPA Project Officer.

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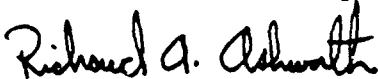
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Although the research described in this report has been funded in part by the United States Environmental Protection Agency under assistance agreement CR-811146 to the University of Oklahoma through in-house research programs, it has not been subjected to the Agency's peer and administrative review and, therefore, may not necessarily reflect the views of the Agency and no official endorsement should be inferred.

This report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including Foreign Nationals.

This technical report has been reviewed and is approved for publication.



RICHARD A. ASHWORTH, Capt, USAF, BSC  
Environmental Research Engineer



THOMAS J. WALKER, Lt Col, USAF, BSC  
Chief, Environics Division



F. THOMAS LUBCZYNSKI, Maj, USAF, BSC  
Chief, Environmental Engineering  
Branch



LAWRENCE D. HOKANSON, Colonel, USAF  
Director, Engineering and Services  
Laboratory

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## SECTION I

### INTRODUCTION

#### A. OBJECTIVE

The primary objective of the research described in this report was to obtain information concerning the biodegradation and sorption of selected organic contaminants in subsurface environments to provide a basis for developing optimal strategies for decontamination of polluted ground water and for predicting the duration and economics of rehabilitation operations.

#### B. BACKGROUND

Within the past few years, pollution of ground water by organic chemicals has come to be recognized as an environmental problem of major proportions. Because ground water serves as drinking water for approximately one-half of the population of the United States and provides about two-thirds of the water used for irrigation (Reference 1), this problem must be addressed to prevent the exposure of humans and sensitive ecosystems to unacceptable levels of potentially harmful pollutants.

Although many organic chemicals have been detected in polluted ground waters, two groups of compounds have been identified with greater frequency, and usually in higher concentrations, than any others. These are chlorinated organic solvents such as trichloroethylene and related compounds; and, hydrocarbon constituents of distilled petroleum products.

Trichloroethylene (TCE) and related low-molecular-weight chlorinated aliphatic hydrocarbons are widely used as solvents and degreasing agents in many industrial and commercial operations. These substances have often been released into the subsurface in relatively large quantities at many locations, primarily through improper waste disposal activities or accidental discharges occurring during transport, storage, and use. The results of such releases are illustrated by an assessment of ground water quality recently conducted in New Jersey (Reference 2). This survey revealed the presence of low-molecular-weight chlorinated hydrocarbons in water from more than a quarter of the 670 wells which were sampled. Many of these substances are possible carcinogens, and maximum contaminant levels (MCL) of 5,5 and 200  $\mu\text{g}\cdot\text{L}^{-1}$  respectively, have been promulgated for TCE, chloroform, and 1,1,1-trichloroethane in drinking water (Reference 3).

Petroleum distillates are used in massive quantities by modern societies as fuels and lubricants. Hydrocarbon fuel constituents have been implicated in numerous incidents of ground water pollution, especially as the result of spills and leaks at service stations, petroleum refineries and storage depots, and airfields. Aromatic hydrocarbons of low to moderate molecular weight, including particularly benzene and its short chain alkyl derivatives, are of special concern. These compounds, which comprise substantial portions of most hydrocarbon fuels, are significantly more water-soluble than most

other constituents of petroleum (Reference 4). Hence, they are leached into ground water in much higher concentrations and migrate through the subsurface with moving ground water much more readily than other petroleum hydrocarbons. Also, a number of these aromatic compounds are known or suspected carcinogens, even at very low concentrations. For example, the  $10^{-6}$  cancer risk level for benzene is  $0.66 \mu\text{g}\cdot\text{L}^{-1}$ , and an MCL for this compound in drinking water of  $5 \mu\text{g}\cdot\text{L}^{-1}$  has been established (Reference 3).

The frequency of ground water pollution incidents involving chlorinated aliphatic hydrocarbon solvents and hydrocarbon fuel constituents, coupled with the potential for adverse health and ecological effects of these substances, has created an urgent need for effective, cost efficient strategies for addressing such incidents. The U.S. Environmental Protection Agency requires such strategies in fulfilling its responsibilities under various legislative mandates, most notably the Resource Conservation and Recovery Act and the Comprehensive Emergency Response, Compensation, and Liability Act. The U.S. Air Force also has a special need for such rehabilitation strategies because investigations performed under the Air Force Installation Restoration Program have identified numerous Air Force facilities with soil and ground water pollution problems involving chlorinated organic solvents and petroleum hydrocarbon fuels.

Ground water rehabilitation strategies usually involve pumping of the polluted water to the surface with subsequent removal of pollutants by air stripping or sorption on activated carbon or other suitable sorbent. Unfortunately, these strategies do not destroy the pollutants, but simply transfer them to another environmental medium (air) or sequester them in a sorbent which must then be properly processed or disposed of to prevent additional pollution problems. Also, because the sorption/desorption of organic pollutants by aquifer solids containing very low levels of native organic matter is not well-understood, it is difficult to predict the volume of water which must be pumped from an aquifer to achieve the required level of contaminant removal and, hence, to accurately estimate the duration and cost of remedial actions employing "pump and treat" strategies.

Strategies utilizing biodegradation for removal of pollutants from ground water also have been employed with some degree of success in addressing ground water pollution incidents, primarily those involving petroleum hydrocarbons. Such biodegradation-based strategies not only have the potential for achieving complete destruction of the pollutants, but also offer the possibility of removing pollutants in situ within the aquifer, without the need to pump the ground water to the surface for treatment. However, further development of these strategies and their possible extension to ground water contamination problems involving other pollutants such as chlorinated hydrocarbon solvents have been impeded by lack of information concerning the nature, extent, and rate of biodegradation of organic pollutants in subsurface environments.

Clearly, improved knowledge of the biodegradation and sorption of chlorinated hydrocarbon solvents and hydrocarbon fuel constituents in subsurface environments would greatly expedite the development of optimized strategies

for addressing ground water pollution problems involving these substances. Such information would provide a basis for: (1) improving and extending the applicability of biological methods for removing these pollutants from ground water, both in situ and in surface treatment systems, (2) devising optimum ground water pumping procedures for recovering such pollutants from contaminated aquifers, and (3) more effectively predicting the time and expense required for rehabilitating aquifers contaminated with these substances. Therefore, the U.S. Air Force Engineering and Services Center (AFESC), Tyndall Air Force Base, Florida, and the U.S. EPA's Robert S. Kerr Environmental Research Laboratory, Ada, Oklahoma (RSKERL), initiated a cooperative research effort in 1983, directed toward the development of a better understanding of the biodegradation and sorption of chlorinated hydrocarbon solvents and hydrocarbon fuel constituents in subsurface environments and the application of this information for developing effective ground water rehabilitation strategies. Under this program, AFESC has provided funding for expansion and focusing of selected RSKERL research efforts of mutual interest to the U.S. Air Force and the EPA. This report describes research conducted at least in part under this program.

### C. SCOPE/APPROACH

The research described by this report consisted of investigations concerned with the biodegradation of organic pollutants by subsurface microorganisms and studies pertaining to the sorption of organic contaminants by subsurface solids. Work in these two major areas of effort was conducted more or less concurrently.

Biodegradation studies were initially concerned with evaluation of the possibility that subsurface microbes growing under aerobic conditions on light aliphatic hydrocarbons might co-metabolically degrade TCE and related compounds which are usually very recalcitrant to biodegradation in aerobic subsurface environments. Laboratory-scale fixed film bioreactors were used to further evaluate this process for possible utility in removing chlorinated organic solvents from ground water pumped from contaminated aquifers. In addition, studies were conducted to evaluate the possibility that light aromatic constituents of hydrocarbon fuels, which have been considered resistant to biodegradation under anaerobic conditions, might undergo biodegradation in anoxic subsurface environments.

Sorption studies were first directed toward development of sorption data for selected aromatic pollutants on a semicontinuous depth series of subsurface materials of low organic carbon content to examine the relative contribution of various physical and chemical properties of the sorbents to sorption of the test compounds. In subsequent works, the sorption of several volatile organic compounds of low polarity on selected low-carbon subsurface materials was evaluated in an attempt to better define the contribution of the mineral surfaces of the aquifer solids to the observed sorption phenomena.

The biodegradation studies are described in Section II below, while those investigations pertaining to organic contaminant sorption are presented in Section III. Conclusions based on this research, including suggestions for additional work, are presented in Section IV.

## SECTION II

### BIODEGRADATION OF CHLORINATED SOLVENTS AND AROMATIC HYDROCARBONS BY SUBSURFACE MICROBES

#### A. BIODEGRADATION OF TRICHLOROETHYLENE AND RELATED COMPOUNDS IN AEROBIC SOILS

Chlorinated organic solvents such as trichloroethylene (TCE), tetrachloroethylene (PCE), and chloroform usually are very resistant to biodegradation in aerobic subsurface environments, which contribute to their persistence in ground waters (References 5,6,7). These compounds undergo biotransformation in anaerobic environments (Reference 8), but these transformations are likely to be incomplete in subsurface materials and may result in the accumulation of products (such as vinyl chloride from PCE and TCE) that are at least as much of a problem as the original contaminant (References 9,10). However, recent reports have indicated that the monooxygenase of methanotrophic bacteria will oxidize and dechlorinate halogenated methanes (Reference 11), and that propane-oxidizing bacteria can epoxidate ethylene, with the resultant epoxide being further metabolized (Reference 12). These reports suggested that the monooxygenases of microorganisms which metabolize low-molecular-weight aliphatic hydrocarbons might also mediate the oxidation of TCE and related compounds, and further indicated the possibility that these pollutants could be biodegraded in aerobic soil systems enriched for such hydrocarbon-utilizing microbes. Obviously, this postulated biodegradation mechanism could serve as a promising basis for developing effective strategies for decontamination of ground water containing chlorinated organic solvents. To investigate this possibility, unsaturated soil was exposed to natural gas to enrich for methanotrophs and for organisms that oxidized the other light hydrocarbons present in natural gas. The capacity of the acclimated soil to remove TCE and similar compounds from infiltrating water was then determined.

##### 1. Materials and Methods

The experimental systems employed for this investigation were very similar to those used at RSKERL in previously reported studies of the behavior of TCE and other organic pollutants in soil profiles (Reference 13). A complete system, consisting of a soil column with associated dosing and sampling components, is shown schematically in Figure 1. The column was a 5 cm i.d. by 150 cm section of borosilicate glass process pipe (Ace Glass, Inc., Vineland, N.J.) packed to a depth of 140 cm with Lincoln fine sand, a mixed, thermic typic ustifluvent. The soil was collected in 10 cm increments from a profile near Ada, Oklahoma, and each increment was packed into the column in the same relative position that it occupied in the parent profile.

Water containing the pollutants to be introduced to the column was stored without headspace in a Teflon®-bag reservoir. The reservoir was connected to the column by Teflon® tubing and was suspended in a closed 20 Liter bottle filled with water. Contents of the reservoir were delivered

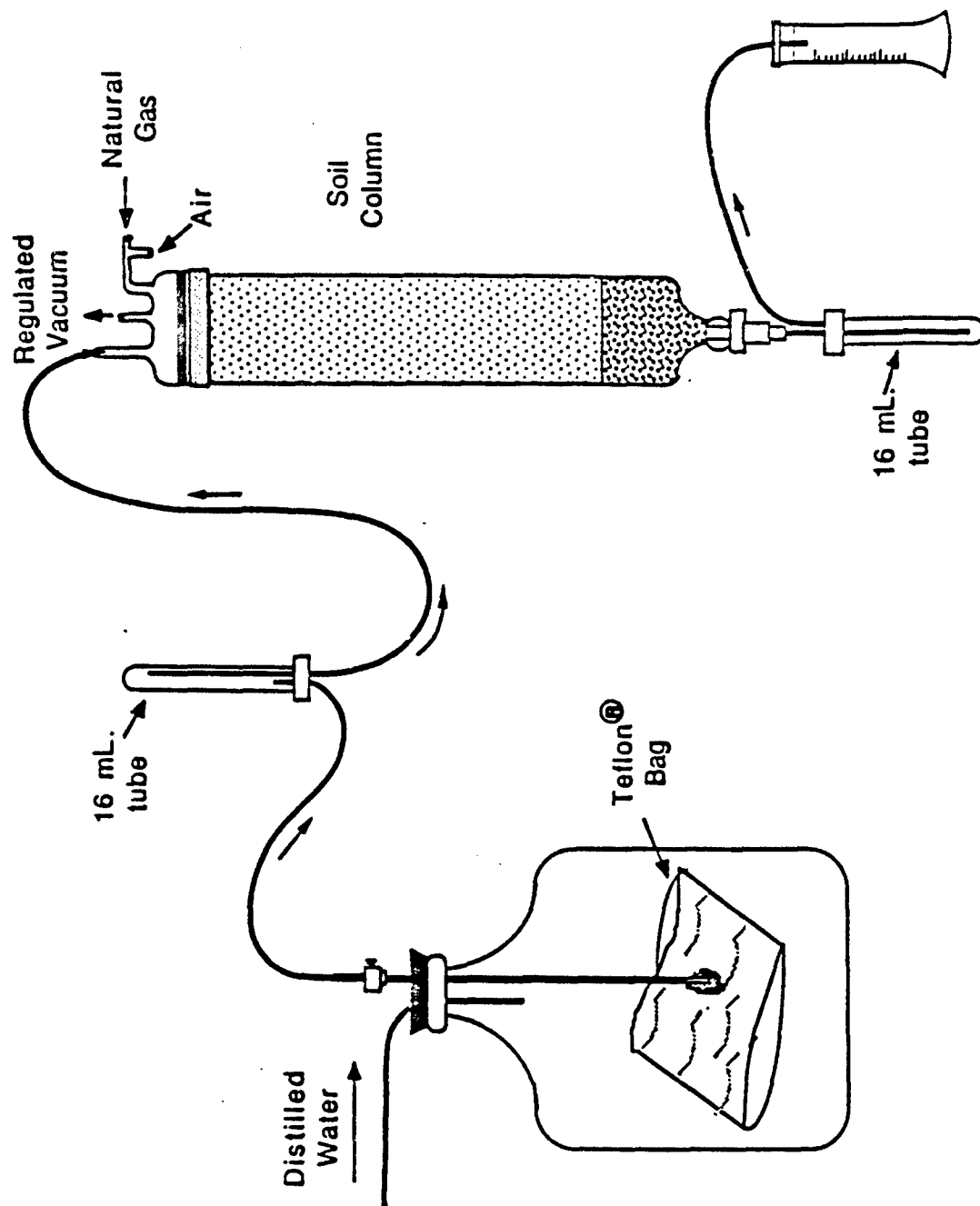


Figure 1. Soil Column System

to the column at a controlled rate by pumping additional water into the closed bottle to compress the Teflon® bag. Before entering the column, the influent solution flowed through a sampling tube consisting of a 16 mL screw-capped test tube sealed with a Teflon®-face septum. The effluent from the column flowed through an identical sampling tube, into a graduated container to permit determination of the total volume of water passing through the column.

A mixture of 0.6 percent natural gas in air (vol/vol) was maintained in the headspace of the columns to enrich the soil for methanotrophs and other microorganisms which oxidatively metabolize light hydrocarbons. The gas was composed of at least 96 percent hydrocarbons, of which 77 percent was methane, 10 percent ethane, and 7 percent propane, with the remainder being mostly butanes and pentanes. Three weeks were allowed for acclimation before introduction of aqueous solutions of chlorinated hydrocarbons to the columns was begun. Water containing the compounds of interest was applied at a rate of 21 cm·day<sup>-1</sup> (410 mL·day<sup>-1</sup>). Since the saturated hydraulic conductivities of the columns used in this investigation were near 150 cm·day<sup>-1</sup>, unsaturated flow conditions were maintained. At appropriate intervals the influent and effluent sampling tubes were removed and their contents were analyzed for chlorinated hydrocarbons using a modified version of U.S. EPA Test Method 624 (Reference 14). In a typical analysis, a 16 mL sample from a sampling tube was mixed with 9 mL of organic-free water. Fluorobenzene (2 µL of a stock solution of 100 ng·mL<sup>-1</sup>) was added as an internal standard, and the 25 mL analytical sample was transferred to the purge vessel of a purge and trap unit (CDS 320-11 sample concentrator, Chemical Data Systems, Oxford, PA). The analytical sample was purged with N<sub>2</sub> at a flow rate of 40 mL·min<sup>-1</sup> for 12 minutes onto a Tenax-GC trap (Chemical Data Systems). The trap was dried of water by blowing N<sub>2</sub> through the trap at 40 mL·min<sup>-1</sup> for 2 minutes with the trap temperature at 40°C. The volatile analytes were desorbed from the Tenax-GC trap by reversing the flow of N<sub>2</sub> through the trap and increasing the temperature to 200°C. The flow rate was 20 mL·min<sup>-1</sup>. The analytes flowed through a transfer line, held at 200°C, onto a fused silica capillary column (0.32 mm by 30 m, SPB-1, 1 µm film thickness, Supelco, Inc., Bellefonte, PA) held at -80°C where they focused at the head of the column. The flow rate of N<sub>2</sub> was reduced to 1 mL·min<sup>-1</sup>. The oven was warmed ballistically to -20°C and then programmed to 100°C at 5°C·min<sup>-1</sup> for separation of the analytes. Analytes were quantified by comparison to standards. A HP 5880A gas chromatograph (Hewlett Packard, Palo Alto, California) was used with an injector temperature at 225°C and a detector (flame-ionization) temperature of 105°C.

## 2. Results and Discussion

In the first phase of the investigation, a column containing soil which had been acclimated to natural gas for 3 weeks was dosed with water containing TCE at an average concentration of 150 µg·L<sup>-1</sup> and the concentrations of TCE in the column effluent were monitored for 2 weeks. The behavior of TCE in the soil exposed to natural gas was compared to that of TCE in an earlier study in which the same soil in the same experimental configuration was dosed with a TCE solution but not exposed to natural gas (Reference 13).



Extensive removal of TCE was observed in the soil exposed to natural gas with less than 5 percent of the applied TCE passing through the column (Figure 2). This is in contrast to results of the earlier study (Reference 13). Without exposure to methane, there was no statistically significant degradation of TCE ( $\alpha=0.05$ ), as inferred from a mass balance of material applied, material that volatilized, and material in the column effluent. As a result, volatilization was the only process in the earlier study, resulting in a mean ( $\pm$ standard deviation) breakthrough of  $28 \pm 1$  and  $21 \pm 13$  percent of the TCE applied at 900 and 180  $\mu\text{g}\cdot\text{L}^{-1}$ , respectively. To confirm that the increased removal in the soil exposed to natural gas represented biological activity, the column was poisoned with water that contained 224  $\mu\text{g}$  of TCE and 2 grams of sodium azide per liter. Breakthrough of TCE increased dramatically (Figure 2) to levels that were seen in the earlier study.

In an attempt to identify the products of the biotransformation, a second column was acclimated to natural gas, then dosed with a solution of  $^{14}\text{C}$ -TCE. After 1.6 elution volumes of water had been applied,  $15.8 \pm 0.3$  percent ( $\alpha=0.05$ ) of the applied radiolabel appeared in the column effluent. When the column effluent was adjusted to pH 11, the radiolabel could not be purged by conditions of vigorous aeration that could remove 99 percent or more of the label from the  $^{14}\text{C}$ -TCE dose solution. At least 95 percent ( $\alpha=0.05$ ) of the label was purged from the effluent when the pH was adjusted to 2, and at least 93 percent ( $\alpha=0.05$ ) of the label precipitated with barium hydroxide. After 2.9 elution volumes, the label in the effluent increased to  $24.6 \pm 0.4$  percent ( $\alpha=0.05$ ) of the applied label. Again, essentially all of it precipitated in the presence of barium hydroxide. Apparently the TCE was degraded to carbon dioxide. Because the soil used in this study had little organic matter (0.4 percent at the surface, 0.04 percent at 150 cm) and essentially no structure, the occurrence of anaerobic microhabitats in the column was unlikely. Hence, the observed degradation was almost certainly an aerobic process.

In the second phase of this study, additional columns acclimated to natural gas were dosed with aqueous solutions containing TCE and 11 other halogenated aliphatic hydrocarbons. Solutions containing mixtures of pollutants in the following concentrations, in  $\mu\text{g}\cdot\text{L}^{-1}$ , were applied: (1) cis- and trans-1,2-dichloroethylene, 170 and 190, chloroform, 210, and 1,2-dibromoethane (EDB), 270; (2) dichloromethane, 270, 1,1-dichloroethane, 240, 1,2-dichloroethane, 280, 1,1,1-trichloroethane, 210, and 1,1,2-trichloroethane, 290; (3) carbon tetrachloride, 1,100, trichloroethylene, 1000, and tetrachloroethylene, 700. Control columns were dosed with solutions containing the same concentrations of halogenated hydrocarbons plus 0.1 percent (wt·vol $^{-1}$ ) sodium azide and were not exposed to natural gas.

The percentages of the 12 halogenated hydrocarbons removed by biodegradation during passage through the columns exposed to natural gas are presented in Table 1. These percentages were calculated from the relative concentrations of each compound in the effluents from the natural-gas-acclimated columns and from the control columns. As Table 1 shows, all compounds evaluated were biologically removed to varying degrees ranging from 19 to > 98 percent. Compounds removed to the greatest extent were

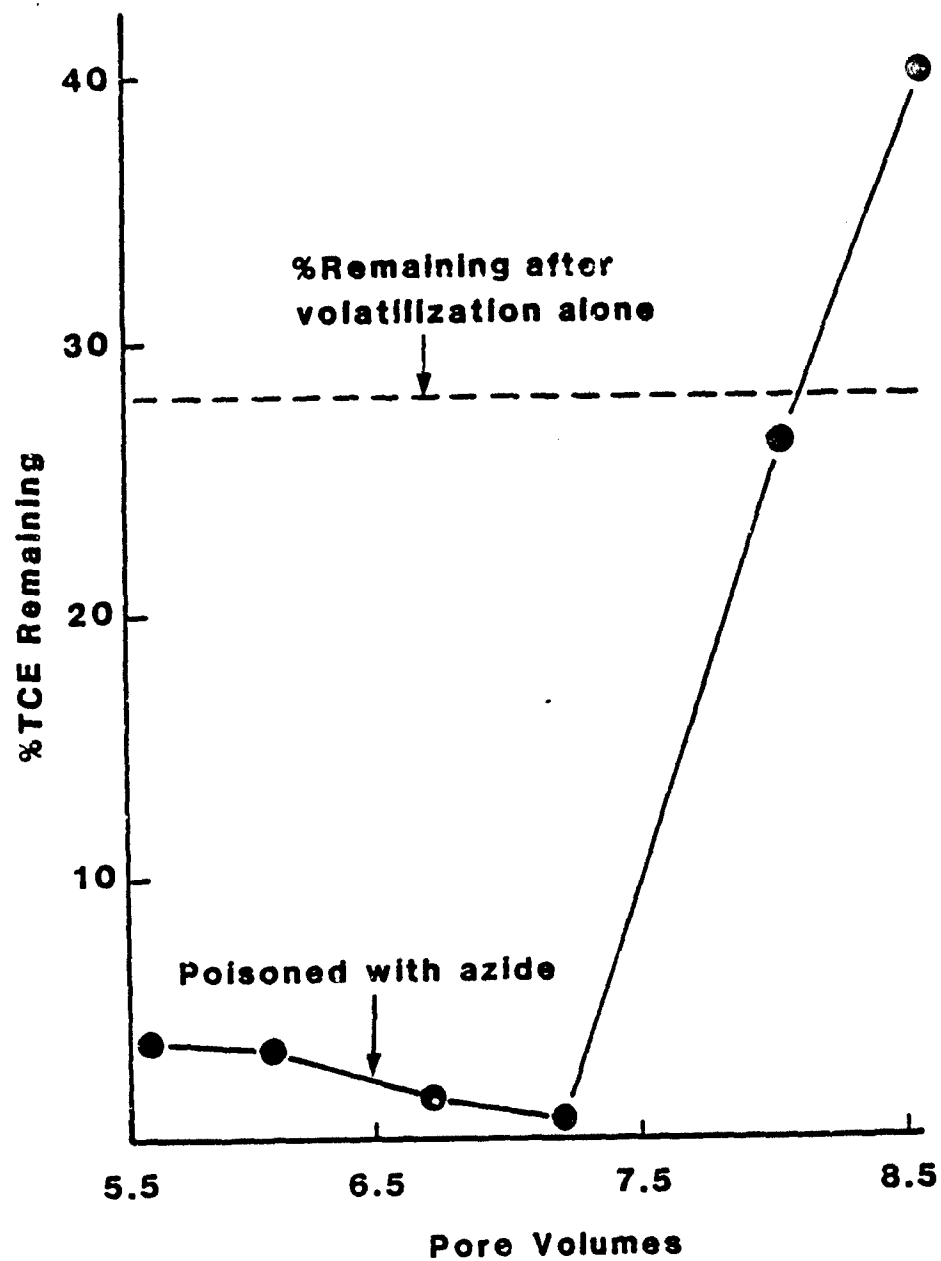


Figure 2. Removal of Trichloroethylene During Passage Through Unsaturated Soil Exposed to an Atmosphere of 0.6 Percent Natural Gas in Air (v/v)

trichloroethylene, cis- and trans-1,2-dichloroethylene, dibromoethane (EDB), and dichloromethane. Carbon tetrachloride, tetrachloroethylene, and 1,1,1- and 1,1,2-trichloroethane were removed to the lowest extent while chloroform, and 1,1- and 1,2-dichloroethane were removed at intermediate levels.

The extent and rate of removal of the hydrocarbons appeared to be related to the molecular structure of each hydrocarbon. For chlorine-substituted methanes (Figure 3), the rate of removal was positively correlated with the increase in the number of carbon-hydrogen bonds. The rate of removal of the chlorine-substituted ethanes seemed to be related to both the number and position of the carbon-hydrogen bonds. The substituted ethanes with two chlorines were degraded faster than those with three chlorines (Table 1, Figure 4). Also, when the chlorine atoms were bonded to each of the two carbon atoms, as opposed to being on the same carbon atom, the rate of removal increased (Table 1, Figure 4). The rate of removal was positively correlated with the ratio of the number of carbon-hydrogen bonds on the Number 1 carbon to the total number of chlorines present. The rate of removal of 1,2-dibromoethane was higher than 1,2-dichloroethane and did not fit onto this curve. This result may be related to the difference in electronegativity between bromine and chlorine. Rates of removal of the chlorine-substituted ethylenes appeared to depend on the number of C-H bonds in the molecule, but a definitive relationship between structure and rate of removal could not be determined, at least in part because the dichloroethylenes were removed below the detection limit.

TABLE 1. MICROBIAL REMOVAL OF HALOGENATED HYDROCARBONS IN SOIL COLUMNS EXPOSED TO 0.6 PERCENT NATURAL GAS IN AIR

Compound	Percent Removed	Rate of Removal (hr <sup>-1</sup> ) <sup>a</sup>
trans-1,2-dichloroethylene	>94	>0.86 (-)
cis-1,2-dichloroethylene	>98	>1.2 (-)
chloroform	83	0.55 (0.29-0.81)
1,2-dibromoethane (EDB)	94	0.86 (0.42-1.3)
dichloromethane	94	0.91 (0.41-1.41)
1,1-dichloroethane	76	0.44 (0.41-0.47)
1,2-dichloroethane	85	0.60 (0.56-0.64)
1,1,1-trichloroethane	19	0.067 (0.023-0.19)
1,1,2-trichloroethane	55	0.25 (0.22-0.28)
carbon tetrachloride	44	0.18 (0.13-0.23)
trichloroethylene	95	0.95 (0.75-1.15)
tetrachloroethylene	31	0.11 (0.085-1.35)

<sup>a</sup>Assumes that the biological activity is uniformly distributed in the top 10 cm of the living soil column. Mean ( $\pm$ 95 percent confidence limits)  $n = 3$ .

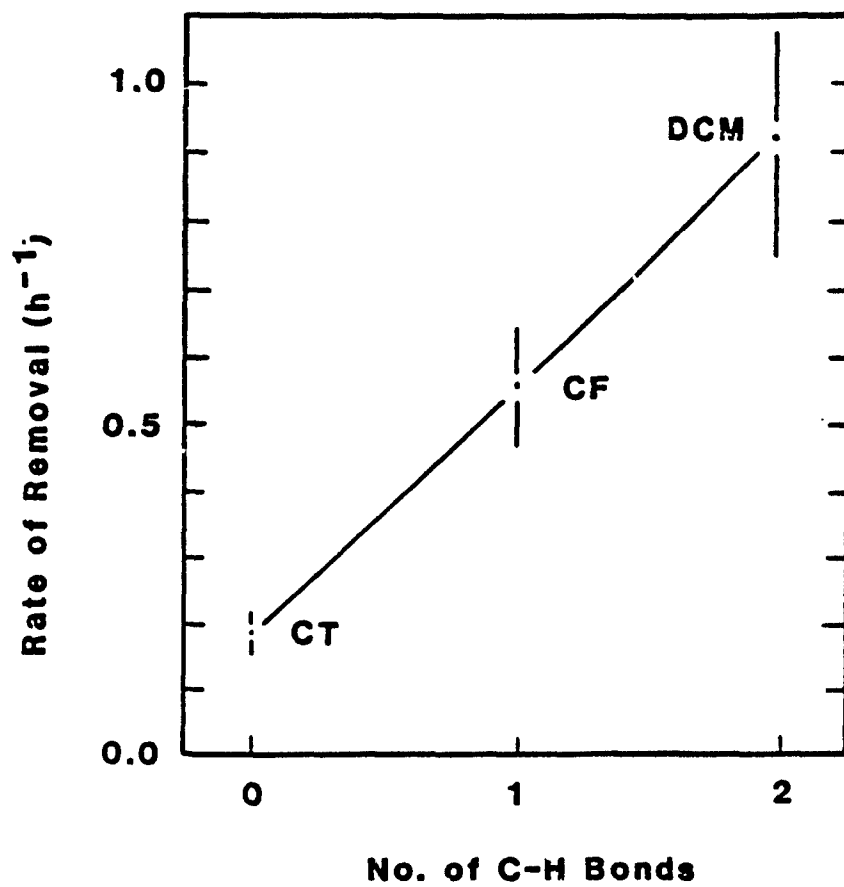


Figure 3. Relationship Between Removal Rate and Number of C-H Bonds for Chlorinated Methanes

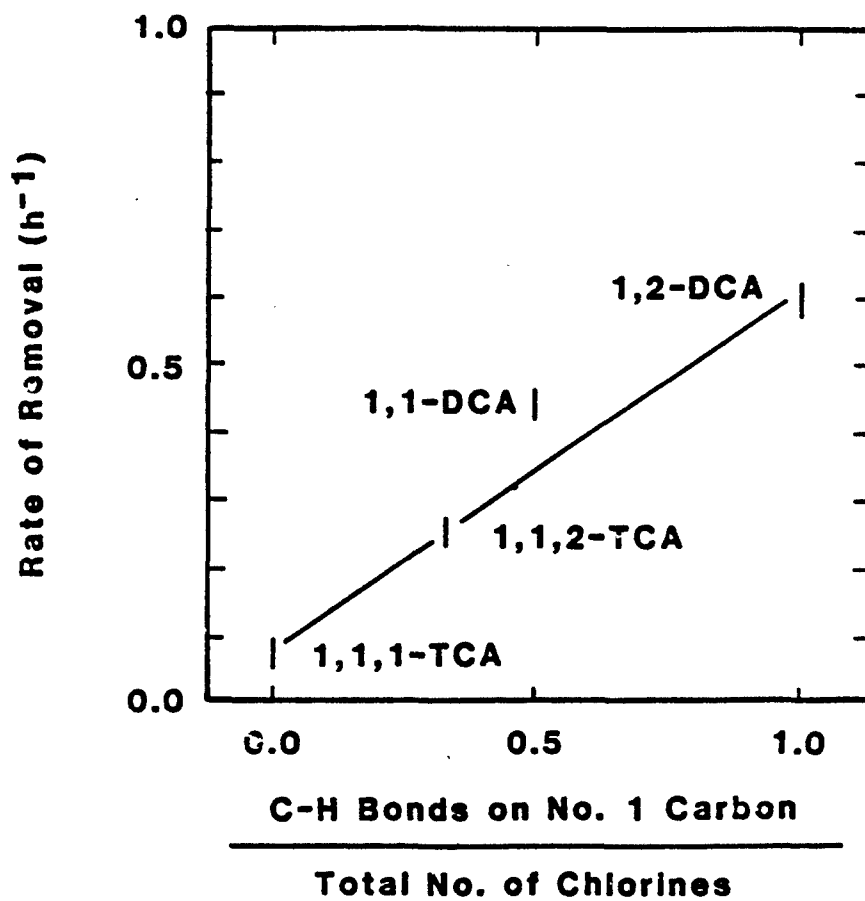


Figure 4. Relationship Between Removal Rate and Number and Position of Substituents of Chlorinated Ethanes.

This investigation showed clearly that the native microbial community of a sandy soil could degrade TCE and several other similar halogenated aliphatic hydrocarbons when stimulated by exposure to 0.6 percent natural gas in air. The observed biodegradation was probably the result of cometabolism of the halogenated hydrocarbons by the methanotrophic bacteria and similar organisms present in the soil which utilized the natural gas as primary substrate for oxidative metabolism. This microbial process should be useful in developing effective strategies for decontamination of ground water polluted by TCE and similar compounds.

#### B. BIODEGRADATION OF CHLORINATED SOLVENT IN A FIXED-FILM BIOREACTOR

The discovery that soil microbial communities supported on gaseous aliphatic hydrocarbons can biodegrade TCE and related compounds opens the possibility of utilizing biodegradation-based strategies for addressing ground water pollution problems involving chlorinated organic solvents. Biological removal of such contaminants in situ within the aquifer is particularly attractive since the necessity for pumping polluted ground water to the surface for treatment would be alleviated. Also, more effective and rapid rehabilitation of contaminated geologic matrices would likely be achieved. This possibility is currently the object of considerable research, particularly at Stanford University, under sponsorship of EPA.

Biological removal of chlorinated hydrocarbon solvents from polluted ground water after it has been pumped to the surface is also an important possibility because, in many circumstances, the geology will not permit successful in situ biological rehabilitation of ground water polluted by TCE and similar compounds. In these situations, it will be necessary to contain the contamination by pumping. In other situations the contamination may be located beneath large industrial facilities or sensitive military installations that would be seriously disrupted or destroyed by activities required for complete rehabilitation of the contaminated geological materials. Under these circumstances, pumping would probably be used to localize the contamination until the facilities have passed their service life and can be taken out of operation to permit comprehensive aquifer restoration activities. In either case, pumping will produce large volumes of ground water containing chlorinated organic pollutants. These must be removed before the water can be reinjected or disposed to surface water. Removal of these substances by biodegradation would be much more effective than removal by the more conventional practices of air stripping and sorption, since the pollutants would be destroyed rather than transferred to the air or to a sorbent requiring further processing. Therefore, an investigation was initiated to examine the utility of fixed film bioreactors containing soil microorganisms supported on gaseous aliphatic hydrocarbons for removing chlorinated organic solvents from ground water pumped from contaminated aquifers. The biodegradation of TCE and 1,1,1-trichloroethene in a laboratory-scale fixed film soil bioreactor utilizing propane as primary substrate was evaluated, and a preliminary appraisal was made of the probable cost of biological removal compared to removal by air stripping and carbon adsorption.

## 1. Materials and Methods

### a. Design of the Bioreactor

A schematic drawing of the bioreactor system is shown in Figure 5. The reactor was constructed in a 5 cm by 150 cm borosilicate glass column. The column was filled with 125 cm of coarse sand. The sand was washed and sieved to pass a Number 10 (2 mm opening) soil sieve and be retained by a Number 16 (1.19 mm opening) soil sieve. Then 10 cm of a mixture of Lincoln fine sand (a mixed, thermic typic ustifluent) and the coarse sand was added to the top of the column. A solution of trichloroethylene and 1,1,1-trichloroethane in spring water was continuously pumped to the head of the column. The water drained by gravity. A mixture of propane in air was supplied to the sealed headspace of the column. A Teflon® vacuum line was buried in the sand to a depth of 100 cm to pull the propane-enriched air through the air-filled spaces of the reactor. The air-filled porosity of the column was 80.5 percent. The Darcy flow through the reactor was 296 cm·day<sup>-1</sup> for water and 800 cm·day<sup>-1</sup> for air (6.0 L of water and 16.6 L of air·day<sup>-1</sup>). The spring water and the Lincoln fine sand have been described in detail in Reference 13.

### b. Operation of the Bioreactor

A concentrated aqueous solution of trichloroethylene and 1,1,1-trichloroethane was prepared by stirring the compounds in a screw-cap Erlenmeyer flask sealed with a Teflon®-faced septum. The concentrated solution was diluted up to 4 Liters and transferred to a large Teflon® bag (B in Figure 5) suspended in water in a large carboy. A peristaltic pump (D) pulled spring water from a reservoir (C), one-third of which pressurized the carboy and forced the solution out of the Teflon® bag to mix with the other two-thirds of the spring water before it went on the column. The influent concentration of trichloroethylene was 820 µg·L<sup>-1</sup>, and that of 1,1,1-trichloroethane was 765 µg·L<sup>-1</sup>.

The peristaltic pump also pulled a slight vacuum on the buried tube mentioned earlier (G in Figure 5). As a result, air was pulled into the sealed headspace (F). The pump also metered the flow of propane from a cylinder (A) to mix with the air entering the headspace of the column.

### c. Sampling the Bioreactor

Before entering the column, the influent water passed through a 16-mL screw-cap test tube (E). This water was sampled to measure the influent concentration of the chlorinated organic compounds. A similar 16-mL screw-cap test tube at the effluent port of the column was used to sample the water effluent. The concentration of the chlorinated organic compounds in the effluent air was measured by inserting a Tenax® resin trap (not shown in Figure 5) just upstream of a soap bubble flowmeter (L) used to monitor flow of air through the column.

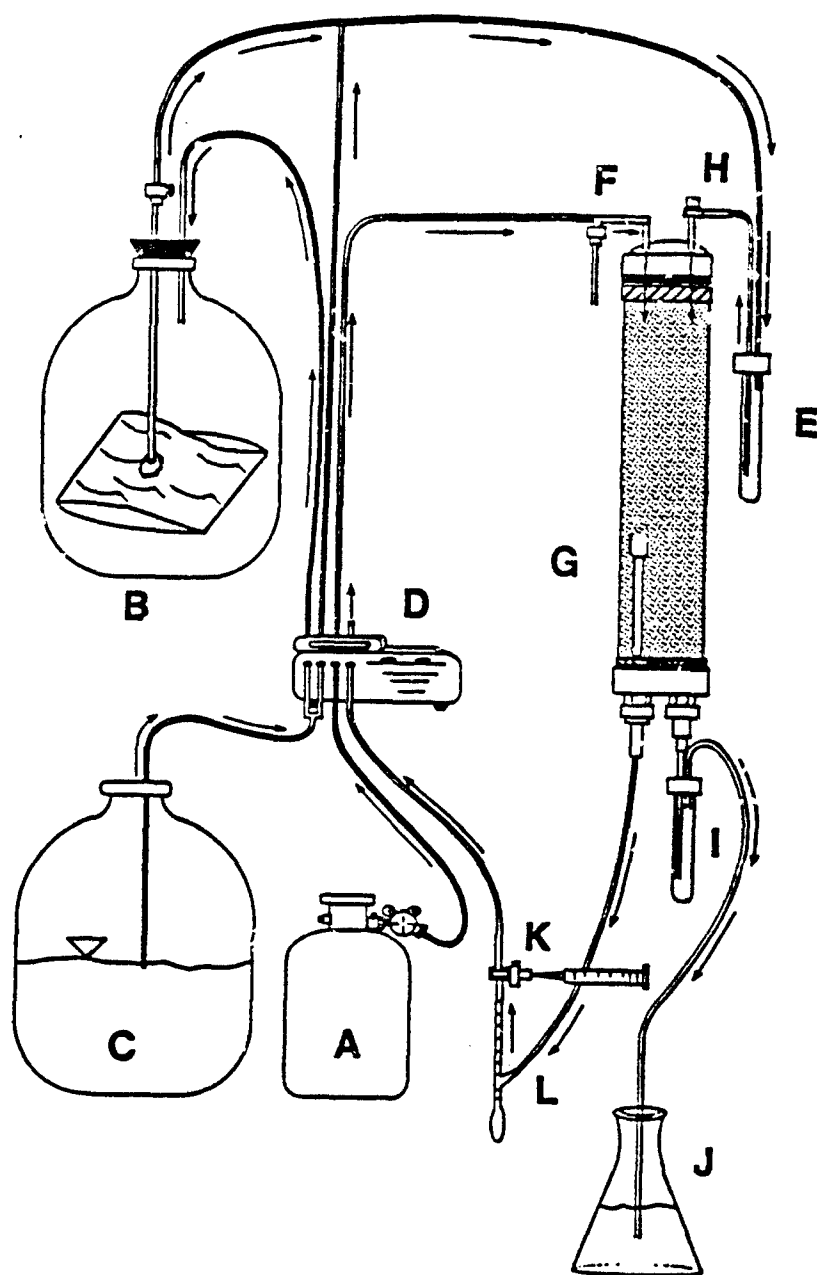


Figure 5. Fixed-Film Soil Bioreactor System.



Propane in the sealed headspace of the column was sampled through a septum (H) with a gas-tight syringe. Propane in the air effluent was sampled through a septum at (K). Propane samples were analyzed according to the method of Mindrup (Reference 15). Water samples and the Tenax® resin trap were analyzed for TCE and 1,1,1-trichloroethane by a modified version of EPA Method 624 (Reference 14).

## 2. Results and Discussion

### a. Biodegradation in the Fixed Film Bioreactor

Initially, the reactor was constructed only of the coarse sand; after 4 weeks, degradation was not observed and, at that time, the soils/sand mixture using the Lincoln fine sand was added because of its previous success in degrading trichloroethylene. Initial acclimation took approximately 2 weeks; significant removals of trichloroethylene in the effluent gas samples were seen on day 13. Extensive removals of trichloroethylene in both effluent gas and water phases were seen thereafter (Table 2). No significant reduction of 1,1,1-trichloroethane was observed in either the effluent gas or water phases (Table 2).

TABLE 2. REMOVAL OF TRICHLOROETHYLENE AND 1,1,1-TRICHLOROETHANE IN A FIXED-FILM BIOREACTOR

Time (days)	Propane		Trichloroethylene			1,1,1-Trichloroethane		
	Quantity Applied (mg·L <sup>-1</sup> )	Fraction Remaining in Air	Fraction Remaining			Fraction Remaining		
			in Air	in Water	Total	in Air	in Water	Total
-----% Influent-----								
1	240	98	42	43	84	57	34	91
5	380	86	48	46	93	74	41	115
7	390	111	44	40	84	64	31	95
11	430	104	38	38	76	54	27	83
13	580	99	3.2	35	38	70	32	102
14	19	16	7.3	3.3	11	56	38	94
15	17	5.3	13	4.5	17	65	34	99
17	NA	NA	4.1	8.3	12	75	43	117
18	15	3.9	NA	NA	NA	NA	NA	NA
19	19	0.85	9.2	9.9	19	52	43	95
21	0	0	0.44	4.5	4.9	73	43	116
22	0		16	23	39	43	36	82
23	0		21	34	54	44	33	77
25	0		40	64	104	60	45	103

The addition of propane to the top of the column was discontinued on day 21 to confirm the removal of trichloroethylene by a cometabolic process of the propane-utilizing microorganisms. Within 4 days, the concentrations of trichloroethylene returned to the original concentrations before acclimation was established.

b. Comparison to Other Systems

Two other studies can be employed to evaluate the performance of the biofilm reactor used in this study. Fogel et al. (Reference 16) and M. Fogel\* studied the degradation of TCE and related compounds by a mixed culture of bacteria supported on methane. In this work, 15 to 25 mL of growing culture were added to fresh media to make a total volume of 50 mL. The culture was then sealed in a 160 mL serum bottle with a Teflon®-faced septum. A syringe was used to withdraw 20 mL of air from the serum bottle and to replace it with 20 mL methane. The chlorinated organic contaminants were injected through the septum and the bottles were shaken until the compounds equilibrated. The concentrations of the chlorinated organics in the cultures were then monitored to detect biodegradation. Killed cultures were also monitored for evidence of nonbiological removal.

Also, the biodegradation of TCE and 1,1,1-trichloroethane in microcosms constructed with aquifer material from the Santa Clara Valley of California (Silicon Valley) was followed in other studies at the R. S. Kerr Environmental Research Laboratory (Reference 17). The pore water of the microcosms was replaced with ground water containing an average of  $82 \mu\text{g}\cdot\text{L}^{-1}$  of 1,1,1-trichloroethane,  $28 \mu\text{g}\cdot\text{L}^{-1}$  of trichloroethylene,  $21 \text{ mg L}^{-1}$  oxygen, and either  $3.6 \text{ mg}\cdot\text{L}^{-1}$  of methane or  $11 \text{ mg}\cdot\text{L}^{-1}$  of propane. After 10 days' incubation at  $17^\circ\text{C}$ , the pore water was sampled, and analyzed for trichloroethylene, 1,1,1-trichloroethane, methane or propane, and oxygen. The pore water was then replaced with fresh ground water amended as described above and incubated for another 10 days, with a total of 12 application and sampling cycles. Some of the microcosms were poisoned with sodium azide to control for nonbiological removal.

The results of these studies and those obtained in the fixed film bioreactor are reported in units that are not directly comparable. It was therefore necessary to develop a general relationship between the extent of transformation of the chlorinated organic compounds and the quantity of methane or propane consumed. For this purpose, it was assumed that the probability of transformation of any individual molecule of a chlorinated organic would not be influenced by the presence of other molecules of the same compound. As a result, transformation should be first-order with respect to concentration of the chlorinated organic compound. Unpublished work at R. S. Kerr Environmental Research Laboratory shows that this assumption holds for trichloroethylene at concentrations below  $1,000 \mu\text{g}\cdot\text{L}^{-1}$ .

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\*M. Fogel, Personal Communication, 1986

It was further assumed that the chance of transformation of any molecule of the chlorinated organic is proportional to the total enzymatic activity of the appropriate alkane mono-oxygenase over the time interval under consideration. As a result, transformation should be first-order with respect to the quantity of primary substrate (methane, propane, or other alkane) consumed in that interval.

The general relationship is as follows:

$$C/C_0 = e^{-kh}$$

where C = final concentration of the chlorinated organic  
 $C_0$  = initial concentration of the chlorinated organic  
h = amount of primary substrate consumed (mg consumed per liter of water treated)  
k = a utilization constant (liters of water treated per mg substrate consumed)

It is important to note that the utilization constant is not a rate constant.

Utilization constants for the biofilm reactor, the aquifer material, and the mixed culture are presented in Table 3. Primary data on final and initial concentrations of the chlorinated organics and on the

TABLE 3. COMPARISON OF THE BIODEGRADATION OF TRICHLOROETHYLENE AND RELATED COMPOUNDS IN DIFFERENT EXPERIMENTAL SYSTEMS

Chlorinated Hydrocarbon	Primary Substrate	Utilization Constant (liter water treated mg <sup>-1</sup> primary substrate consumed)			
		Biofilm Reactor	Aquifer Material <sup>a</sup>	Mixed-Culture <sup>b</sup>	Mixed-Culture <sup>c</sup>
1,1,1-Trichloroethane	Propane	<0.004	0.19 <sup>d</sup>		
Trichloroethylene	Propane	0.120 0.099 0.129 0.081	0.073		
1,1,1-Trichloroethane	Methane		0.15		
Trichloroethylene	Methane		0.075	0.05	0.085
1,1-Dichloroethylene	Methane			0.02	
Cis-1,2-Dichloroethylene	Methane			>0.3	
Trans-1,2-Dichloroethylene				>0.3	
Vinyl Chloride				>0.3	

<sup>a</sup>Reference 17

<sup>b</sup>Reference 16

<sup>c</sup>Fogel, M., Personal Communication, 1986

<sup>d</sup>After acclimation; before acclimation the utilization constant was <0.04

amount of primary substrate consumed were used to calculate the utilization constants for the biofilm reactor and the aquifer microcosms. The amount of methane used by the mixed cultures reported in Fogel et al. (Reference 16) was estimated from the initial protein concentrations of the culture, and the assumptions were: (1) the cells were 50 percent protein, (2) the biomass doubled during the incubation, (3) the elemental composition of the biomass was  $C_5H_7O_2N$ , and (4) two-thirds of the total methane consumed went to biomass. The methane consumed by the the mixed cultures described by M. Fogel\* was estimated from the actual increase in optical density of the culture, rather than simply assuming that the biomass doubled.

The utilization constants for trichloroethylene biodegradation are suprisingly consistent across the three systems. Biodegradation of trichloroethylene supported on propane is very similar in the biofilm reactor and the aquifer material, and trichloroethylene degradation supported on methane is very similar in the aquifer material and the mixed-culture studies.

Unfortunately, the biodegradation of 1,1,1-trichloroethane is not as predictable. The biofilm reactor failed to remove 1,1,1-trichloroethane while removals in the aquifer material were extensive. The reason for the difference in behavior is not known.

Both cis-1,2-dichloroethylene, trans-1,2-dichloroethylene, and vinyl chloride are commonly encountered in ground water originally contaminated with trichloroethylene (Reference 10). The high utilization constants for cis-1,2-dichloroethylene, trans-1,2-dichloroethylene, and vinyl chloride in the mixed-culture grown on methane suggest that these compounds can be removed as the water is cleansed of trichloroethylene.

#### c. Preliminary Economic Analysis

The utilization constants can be used to estimate the quantity of primary substrate required to produce any desired level of treatment. This permits a preliminary analysis of the economic feasibility of biological treatment of waters contaminated with trichloroethylene and related compounds (Table 4). In the spring of 1986 in Central Oklahoma, both propane and natural gas delivered to commercial customers cost about  $\$0.24\text{-kg}^{-1}$ . For high-volume users, natural gas becomes cheaper, but gas requires a distribution network while propane can be trucked to the point of use.

A price of  $\$0.24\text{-kg}^{-1}$  for natural gas or propane and the utilization constants from Table 3 were used to estimate the cost of reducing the concentration of trichloroethylene, 1,1-dichloroethylene, or 1,1,1-trichloroethane from  $1,000\text{ }\mu\text{g}\cdot\text{L}^{-1}$  to  $5\text{ }\mu\text{g}\cdot\text{L}^{-1}$ . The Maximum Contaminant Levels proposed under the Safe Drinking Water Act for these compounds are 5, 7, and  $200\text{ }\mu\text{g}\cdot\text{L}^{-1}$ , respectively (Reference 3).

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\*M. Fogel, Personal Communication, 1986

TABLE 4. ESTIMATED COST TO REDUCE CONCENTRATION OF ORGANIC CONTAMINANTS FROM 1,000 to  $5\mu\text{G}\cdot\text{L}^{-1}$

	<u>Estimated Cost, Cents per 1,000 Gallons</u>			
	Air Stripping <sup>a</sup>	Carbon Adsorption <sup>b</sup>	Biodegradation Supported on	
			Propane	Methane <sup>c</sup>
Trichloroethylene	1.0	46	4.1 <sup>d</sup>	6.5
1,1-Dichloroethylene	1.0	163	No Data	19.6
1,1,1-Trichloroethane	1.1	125	119 <sup>d</sup> to 2.5 <sup>e</sup>	3.2

<sup>a</sup>Total cost, estimated from Figures B-1, B-3, and B-9 of Javandel et al. (Reference 18).

<sup>b</sup>Total cost, estimated from Appendix D, Javandel et al. (18). Because the mean adsorption capacity of activated carbon for trichloroethylene and carbon tetrachloride are similar, figures reported for carbon tetrachloride are used to estimate cost for trichloroethylene.

<sup>c</sup>Cost of natural gas alone, based on utilization constants for trichloroethylene and 1,1,1-trichloroethane derived from the data of Henson et al. (19), and a constant for 1,1-dichloroethylene derived from the data of Fogel et al. (16).

<sup>d</sup>Cost of propane alone, based on utilization constants derived in this study.

<sup>e</sup>Cost of propane alone, based on utilization constants derived from the data of Henson et al. (Reference 19).

The data in Table 4 indicate that biological treatment will be somewhat more expensive than air stripping, but it should compete with carbon adsorption. The cost of the primary substrate is only about one-tenth the total cost of carbon adsorption. If small, inexpensive bioreactors with low power requirements can be designed, the total cost of biological treatment should compare quite favorably with carbon adsorption.

Based on the constants in Table 3, the extent of treatment of trichloroethylene is reasonably predictable. Unfortunately, removals of 1,1,1-trichloroethane vary widely between systems. Until the factors that promote 1,1,1-trichloroethane removal are identified, it will be impossible to expect biological treatment systems for 1,1,1-trichloroethane to perform according to design expectations.

### C. BIODEGRADATION OF AROMATIC HYDROCARBONS IN ANOXIC AQUIFER MATERIALS

As mentioned previously, aromatic hydrocarbons such as benzene and its short-chain alkyl derivatives are present in significant quantities in most distilled petroleum products. In a recent study (Reference 4), the major constituents of unleaded gasoline, kerosene, and Number 2 fuel oil and their respective water-soluble fractions were identified. Aromatic compounds comprised a maximum of 50 percent of the weight of the original products, but in every case greater than 93 percent by weight of the water-soluble fraction was composed of aromatics. Because low-molecular-weight aromatic compounds are much more soluble in water than the other constituents of petroleum, and because they do not sorb onto subsurface solids to a significant degree, they are found dissolved in and migrating with moving ground water to a much larger extent than other components of petroleum distillates.

Aromatic hydrocarbons of low molecular weight have been shown to degrade rapidly in aerobic subsurface environments (References 20,21), but little attention has been given to the possibility that these compounds might have a biological fate in anoxic aquifers. If benzene and its alkyl derivatives were found to degrade in anoxic aquifers, strategies for addressing ground water contamination problems involving distilled petroleum products could be significantly affected. To further evaluate this possibility, the behavior of benzene and several of its alkyl derivatives in anaerobic subsurface environments was investigated, employing laboratory microcosms constructed from authentic anoxic aquifer materials.

#### 1. Materials and Methods

##### a. Aquifer Materials

The anoxic aquifer materials used for these studies were obtained at a closed landfill near Norman, Oklahoma, and at the site of an aviation gasoline spill at the U.S. Coast Guard Air Station near Traverse City, Michigan.

The landfill is located over highly permeable alluvium composed of silt, sand, clay, gravel, and dune sand on the north bank of the South Canadian River. The depth of the alluvium in the area varies from 10.7 to 12.2 meters and the water table averages from 0.6 to 1.5 meters below the original land surface. Municipal refuse was deposited at this site for approximately 60 years before closure. An earlier study pertaining to the effects of this landfill on ground water quality indicated that the refuse was contributing many organic pollutants, including low levels of alkyl benzenes, to the local ground water (Reference 22).

Anoxic aquifer material for construction of microcosms was acquired from a subsurface region adjoining the Norman landfill that was known to be actively methanogenic (Reference 23). Solid samples were obtained by digging down to the region of methanogenesis and scooping up the aquifer material into sterilized 1-quart glass canning jars. Liquid samples were taken by allowing the hole to fill with water and collecting

the water in sterile glass containers. Because of the nearness of the water table to the surface, the aquifer is probably inoculated with surface organisms during every recharge event, and it was not considered necessary to acquire aseptic subsurface samples. The redox potential (Eh) of the aquifer material was measured in a glovebox under nitrogen. A slurry of one part aquifer material was made in five parts deaerated, deionized water (by volume). The Eh of the stirred slurries was monitored continuously over a period of several hours using a wax-impregnated graphite electrode. The equilibrium Eh (vs. Ag/AgCl) of the material was, thus, determined to be -330 mv. The pH of aquifer water from the methanogenic region was 7.3. The relatively high conductivity ( $6000 \mu\text{mhos}\cdot\text{cm}^{-1}$ ) and total organic carbon ( $344 \text{ mg}\cdot\text{L}^{-1}$ ) of this water reflected the influence of the landfill.

The Coast Guard Air Station is situated on lacustrine glacial deposits consisting of an upper sand and gravel unit and an underlying clay unit. The sand and gravel unit contains an extensive plume of ground water contaminated with relatively high concentrations (up to  $30 \text{ mg}\cdot\text{L}^{-1}$ ) of alkylbenzenes. This plume is the result of the accidental release of 2,500 gallons of aviation gasoline into the shallow water table aquifer caused by the failure of a flange on an underground storage tank. It is located in a saturated region of the sand and gravel unit about 15 meters deep, with the water table varying from about 3.6 to 5.5 meters below the land surface. Extensive geochemical characterization of ground water in the region of the plume, conducted as part of a joint EPA-Coast Guard investigation, revealed that anoxic conditions generally prevailed within the plume, and also suggested that methanogenesis was probably occurring therein (Reference 24).

Aquifer material for microcosm construction was acquired from a region of the contaminant plume at Traverse City lying between 7 and 7.6 meters below the land surface. The aquifer solids were obtained by screwing an auger into the ground to the desired depth and carefully lifting it out with a winch so that the structure of the samples was maintained. Aquifer material was transferred from the auger flights to sterile glass jars for transport to the laboratory. Ground water from the region of sample acquisition contained no detectable oxygen and had a pH and Eh of 6.5 and -150 mV, respectively. The conductivity was  $360 \mu\text{mhos}\cdot\text{cm}^{-1}$  and the total organic carbon content was  $10 \text{ mg}\cdot\text{L}^{-1}$ .

#### b. Microcosms

All steps in construction of the anoxic microcosms were performed in an anaerobic glove box to ensure maintenance of anoxic conditions in the aquifer material, and all equipment in contact with the aquifer material was sterilized.

For construction of microcosms from the methanogenic aquifer materials obtained from the Norman landfill, the solids were slurried by the addition of 15 percent by weight aquifer water and then were poured into 160-mL serum bottles, resulting in approximately 100 grams of aquifer material (wet weight) in each experimental unit. The dry weight of the solids averaged

67.5 grams. A dosing solution was prepared by adding benzene, toluene, ethylbenzene, and *o*-xylene together (without a carrier) to autoclaved reverse osmosis water and then stirring the water overnight without a headspace. The microcosms were dosed by the addition of 2.0 mL of the dosing solution after the lip of each bottle had been wiped clean with a sterile wipe. Each unit was sealed with a Teflon®-coated silicone septum and a crimp cap seal immediately after dosing. Sterile controls were prepared by autoclaving microcosm units overnight at 121°C before dosing. The microcosms were maintained inverted in the dark at 17°C, the average temperature of ground water from shallow aquifers in central Oklahoma, until they were analyzed. In addition to the microcosms containing the living and autoclaved aquifer material, a set of serum bottles containing only autoclaved reverse osmosis water plus dosing solution were prepared and carried through the entire experimental procedure to provide additional control for the study.

Microcosms constructed from the anoxic aquifer material obtained at Traverse City were prepared essentially as described above, except that the solids (90-gram wet weight) were not slurried before introduction to the serum bottles. These systems were dosed with a solution containing benzene, toluene, *o*-xylene, and *m*-xylene, and sterile controls were prepared by autoclaving for 1 hour on 2 consecutive days at 121°C before addition of the dosing solution. To further preclude the possibility of oxygen gaining entry, the stored microcosms were maintained in an anaerobic jar under a nitrogen atmosphere until analyzed. These microcosms were maintained at 12°C, the ground water temperature at Traverse City when the aquifer material was obtained.

#### c. Analysis of Microcosms

Two to four replicate microcosms from each treatment (living, autoclaved, or autoclaved water) were analyzed for alkyl benzenes at each sampling interval during the course of the experiments. After addition of an internal standard (1-chlorohexane), the microcosms were sampled by purging the volatile compounds onto a trap (Figure 6). For purging, each unit was attached by means of Teflon® tubing and Swagelok fittings to a stainless steel trap (11.5 cm by 0.4 cm i.d.) packed with Tenax® resin or Tenax®/Silica gel (2:1). The microcosms were placed on a rotary shaker to keep the aquifer material well-slurried during purging. The units were purged with nitrogen at a flow rate of 50 ml·min<sup>-1</sup> for 15 minutes which resulted in purging efficiencies of at least 99 percent for the compounds studied.

The purged compounds were analyzed by a modified version of EPA Method 624 (Reference 14). The traps were desorbed at 180°C for 8 minutes onto the head of a 1.8 meters by 2 mm inside diameter glass column packed with 60/80 Carbopack® C/0.2 percent Carbowax® 1500. The column was held at an initial temperature of 40°C for 8 minutes, then programmed at 8°C·min<sup>-1</sup> to 170°C, and finally held at this maximum temperature for an additional 15 minutes. A Hewlett-Packard 5880A gas chromatograph was used for most analyses, but a Finnigan Model 4000 GC/MS system interfaced with an INCOS data system was employed in some cases to confirm identities of purged compounds.



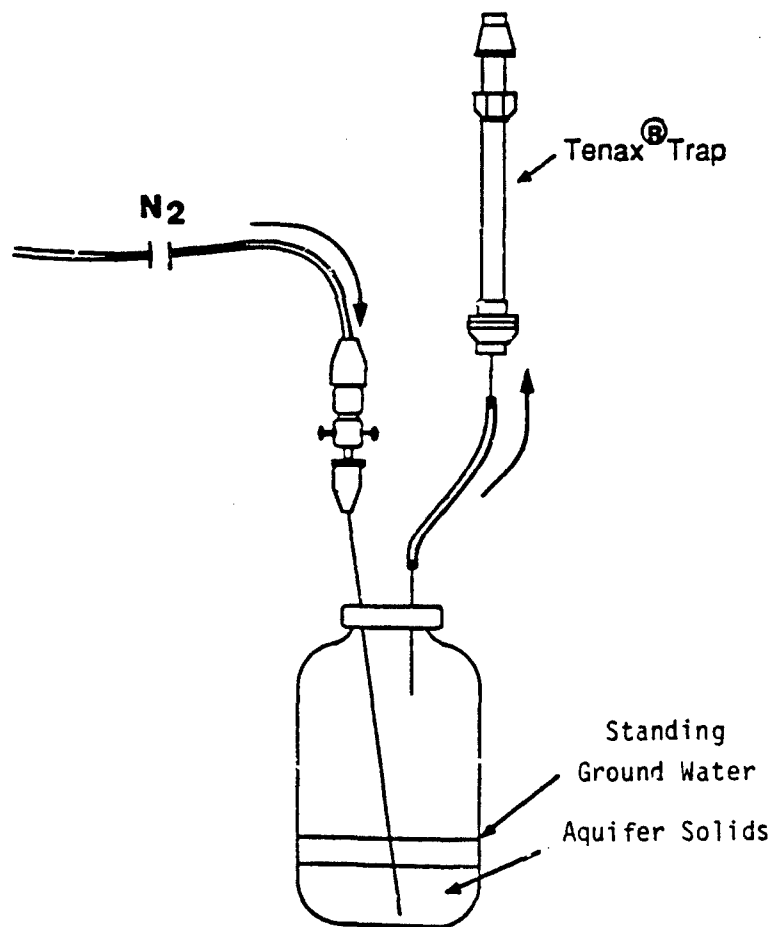


Figure 6. Purging System for Microcosms

## 2. Results and Discussion

The most extensive experiments of this study were conducted using microcosms constructed from the methanogenic aquifer material obtained at the Norman landfill. The principal results of this work are presented in Table 5. As these data show, benzene and the three alkylbenzenes all disappeared in the methanogenic aquifer material. Disappearance was not rapid; long lag times were required before significant removals of all compounds except toluene. Within the first 6 weeks of incubation, toluene concentrations were reduced to 13 percent of the original concentrations in the living microcosms. Benzene, ethylbenzene, and o-xylene were not significantly degraded during the first 20 weeks of incubation. However, after 40 weeks of incubation, the concentrations of benzene, ethylbenzene, and o-xylene were reduced to 28 percent, 26 percent, and 22 percent of the original material. At 120 weeks of incubation, the concentrations of all four compounds were

TABLE 5. BEHAVIOR OF ALKYL BENZENES IN METHANOGENIC AQUIFER MATERIAL FROM A LANDFILL

ug·L <sup>-1</sup> in pore water							
Compound	week 0 <sup>a</sup>	week 6	week 12	week 20	week 40	95%CI <sup>b</sup>	week 120
Living Aquifer Material							
benzene	613	438	499	491	174	474-64	1.6
toluene	547	73	115	92	2.9	17-0.48	1.5
ethylbenzene	269	218	224	238	69	95-50	1.3
o-xylene	257	215	192	204	56	122-26	1.2
Autoclaved Aquifer Material							
benzene	613	770	645	796	634	768-524	426
toluene	547	692	588	672	489	632-379	368
ethylbenzene	269	297	277	264	222	288-172	197
o-xylene	257	310	278	246	230	310-170	171
Autoclaved H <sub>2</sub> O							
benzene	613	689	630	776	530	618-454	- <sup>c</sup>
toluene	547	747	656	753	460	487-452	-
ethylbenzene	269	327	313	328	218	295-188	-
o-xylene	257	326	330	314	221	243-200	-

<sup>a</sup>The concentrations at Week 0 are averages of all dosed microcosms.

<sup>b</sup>95% confidence interval on average at Week 40.

<sup>c</sup>(-) Not analyzed.

reduced to less than 1 percent of the original concentrations in the living samples. In contrast, there was no evidence of loss of benzene, toluene, ethylbenzene, or *o*-xylene in the autoclaved aquifer material at the 40-week interval. By 120 weeks of incubation the concentrations in the autoclaved samples for benzene, toluene, ethylbenzenes, and *o*-xylene were 70 percent, 67 percent, 73 percent, and 66 percent of the original concentrations. Analysis of gases in the headspace of the microcosms at Week 40 revealed the presence of significant levels of methane in the living systems, while no methane was detected in the autoclaved control units. This indicated that methanogenic conditions were maintained in the living microcosms throughout the study.

Degradation products of toluene were examined by dosing microcosms constructed from freshly collected methanogenic aquifer material from the landfill with an aqueous solution of  $^{14}\text{C}$ -toluene. Samples of pore water from the microcosms were analyzed after 6 weeks of incubation. The pore water was poured from the bottles and centrifuged to remove particulates. The pore water was counted for radiolabel, then purged with  $\text{N}_2$  at pH 11, and counted again. Only 5 percent of the total radioactivity was removed by purging, indicating that no more than 5 percent of the radiolabeled material remaining in the pore water was toluene. The disappearance of toluene was also confirmed by gas chromatography, using the previously described methods.

After a pH adjustment to 2, virtually all of the radiolabel could be removed by vigorous purging with  $\text{N}_2$ . To confirm the presence of radiolabeled carbon dioxide, barium hydroxide was added to other samples of pore water, which were shaken, centrifuged, and counted. Approximately half of the radioactivity was removed in the precipitate, confirming  $^{14}\text{CO}_2$  as a primary degradation product. Although the products of transformation were mostly purgeable, a very small percentage of the label remained in the water and would not purge at any pH, indicating the probable formation of a water-soluble, nonpurgeable transformation product of toluene.

The results of the experiment with anoxic aquifer material from the hydrocarbon plume at Traverse City are presented in Table 6. Initial concentrations and concentrations at various incubation times are presented for benzene, toluene, and *o*- and *m*-xylene in pore water of living and autoclaved microcosms constructed from this material. The data indicate relatively rapid removal of all four compounds in the living microcosms, with little or no lag time being required before removal began. After 4 weeks of incubation, concentrations of benzene, toluene, and *o*- and *m*-xylene were 13, 3, 16, and 10 percent, respectively, of the concentrations originally introduced to the microcosms. After 8 weeks the respective concentrations had been further reduced to 10, 1, 4, and 2 percent of initial concentrations. In contrast, concentrations remaining in the autoclaved microcosms after 4 weeks were 57, 61, 49 and 46 percent, of initial concentrations of benzene, toluene, and *o*- and *m*-xylene, respectively. Hence, biodegradation appeared to be primarily responsible for the rapid disappearance of benzene and its three alkyl derivatives in the anoxic aquifer material. This was further confirmed by analyses of headspace gas in the microcosms immediately before sampling for the aromatic compounds. Methane was found in all the living

TABLE 6. BEHAVIOR OF ALKYL BENZENES IN ANOXIC AQUIFER MATERIAL FROM AN AVIATION GASOLINE PLUME

µg·L<sup>-1</sup> in pore water

Compound	week 0	week 2	week 4	week 8
Living aquifer material				
benzene	450	- <sup>a</sup>	12	6
toluene	420	-	56	40
o-xylene	410	-	41	6
m-xylene	440	-	78	17
Autoclaved aquifer material				
benzene	420	380	240	- <sup>a</sup>
toluene	380	290	230	-
o-xylene	370	190	180	-
m-xylene	370	200	170	-

a. (-) Not analyzed.

microcosms in concentrations ranging from 50 to 100 ppm, while no methane was detected in the autoclaved units.

The relatively extensive biodegradation of benzene and various alkylbenzenes that occurred in the anoxic aquifer materials from two different locations during these studies was somewhat surprising, particularly since aromatic hydrocarbons have generally been considered to be recalcitrant to biological action in the absence of molecular oxygen (Reference 25) or oxygen-containing substituent groups (References 26, 27). However, data obtained by others in several recent field and laboratory studies support the observations reported herein. Benzene and toluene were observed as intermediate metabolites during the biotransformation of benzoate and ferulate to methane and carbon dioxide by methane fermentation (Reference 28). Preferential removals of *o*-, *m*-, and *p*-xylene over other petroleum hydrocarbons in a plume of methanogenic landfill leachate indicated that biotransformation of the alkylbenzenes was probably occurring in the anoxic subsurface environment (Reference 29). Removal of the three xylene isomers was also observed under anoxic denitrifying conditions in a laboratory column simulating saturated flow conditions typical for a river/ground water infiltration system (Reference 30). In addition, toluene and benzene apparently were metabolized to carbon dioxide by a methanogenic consortial in a laboratory study which confirmed the incorporation of oxygen from water into the benzene ring in mixed methanogenic cultures (Reference 31).

The potential for anaerobic biotransformation of low-molecular-weight aromatic hydrocarbons in subsurface environments as revealed by this research has significant implications for addressing ground water pollution problems involving distilled petroleum products. Both aerobic and anaerobic degradation of aromatic contaminants within the aquifer must be considered in predicting the impact of a release of petroleum distillates into the subsurface on ground water quality. Otherwise, this prediction is not likely to provide a meaningful basis for selecting the appropriate type and extent of remedial action. Also, the observed anaerobic biotransformation of aromatic hydrocarbons may provide the basis for developing improved or alternative biological methodologies for renovation of ground water contaminated with benzene, alkylbenzenes, and similar compounds leached from distilled petroleum products.

## SECTION III

### SORPTION OF ORGANIC POLLUTANTS ON SUBSURFACE MATERIALS

#### A. SORPTION OF ORGANIC COMPOUNDS ON A LOW CARBON SUBSURFACE CORE

Previous studies by a number of investigators have shown the dependency of organic contaminant sorption on the natural organic carbon content of a variety of soils and sediments (References 32, 33, 34, 35). The result has been a plethora of empirical relationships between organic-carbon normalized sorption and properties of the sorbate, predominantly solubility and octanol-water partition coefficient. Although regression parameters for these relationships will vary, depending on the selection of sorbates and experimental conditions (Reference 36), the relationships are useful in predicting, often within a factor of two, the degree of association of a given sorbate and soil.

Mingelgrin and Gerstl (Reference 37) have discussed the importance of organic pollutant sorption other than hydrophobic sorption to soil constituents. Hassett et al. (Reference 38) and Karickhoff (Reference 39) have developed relationships for predicting conditions when mineral contributions begin to affect sorption of organic pollutants. Working with the limited data available, Karickhoff (Reference 39) has attempted to formulate a model that considers organic carbon blockage of mineral sorption contributions. For nonpolar compounds, mineral sorption processes are secondary to hydrophobic effects in most sediments and soils. However, in the low carbon environments characteristics of the subsurface, mineral sorption may affect pollutant mobility and contribute to the costs of aquifer restoration and other cleanup efforts. To further evaluate this possibility, a study was initiated of the sorption of selected aromatic compounds by a semicontinuous depth series of subsurface samples. The primary objective of this research was to examine the relative contribution of various physical and chemical properties of the subsurface material to the sorption of these compounds. A secondary objective was to evaluate and optimize methodology for determining sorption of organic compounds on subsurface solids of low sorptive capacity.

##### 1. Materials and Methods

###### a. Acquisition and Characterization of Core Material

Subsurface solids were obtained from a river alluvial plain near Lula, Oklahoma, using an augered drilling rig fitted with custom-made 10 cm diameter nickel-plated mild steel core barrels. Cores were taken by pressing the length of the core (50 cm) into the ground, extracting the core, redrilling the hole to the estimated base of the core, then collecting the next core. Cores were hydraulically extruded into polyethylene bags; where changes in the strata were apparent within a core, cores were split. The result was a series of 20 samples collected over a total depth of 675 cm. All core samples were air-dried, ground with mortar and pestle and passed through an 18-mesh sieve (1 mm openings). These samples were stored at room temperature and used for soil characterization and sorption isotherm studies.

Total organic carbon (TOC) was determined by a modified combustion method using the following procedure. One-gram oven-dried (105°C for 24 hours) samples in porous porcelain crucibles were placed in 50 mL beakers and 12 mL 5 percent HCl added. After leaching overnight, the contents were exhaustively washed with carbon-free distilled water pulled through the crucible with a light vacuum. The washings were collected, purged of CO<sub>2</sub> and analyzed on a Beckman Model 915 Total Organic Carbon Analyzer. The contents of the crucible were oven-dried at 105°C overnight and analyzed on a Leco Model WR12 Carbon Analyzer. The results of the two analyses were combined to yield TOC. The method yields acceptable results down to about 0.1 percent TOC; below this level standard deviation of replicates increases significantly.

Cation exchange capacity (CEC) was estimated, using an ammonia electrode procedure (Reference 40). Standard methods of soil analysis were used for determining soil particle density, particle size distribution (Hydrometer Method), and pH (Reference 41). Surface area was estimated using the ethylene glycol monoethyl ether (EGME) technique (References 42, 43).

b. Determination of Partition Coefficients and Sorption Isotherms

The compounds used in this study were o-chlorotoluene (OCT), 1,2,4-trichlorobenzene (TCB), and dimethylphthalate (DMP). These compounds were obtained labeled with <sup>14</sup>C from Pathfinders Laboratories, Inc., St. Louis, Missouri, with specific activities of 9.0, 16.1, and 10.6 mCi·mmole<sup>-1</sup>, respectively. The log octanol-water partition coefficients (log KOW values) employed for this work are as follows: 4.26 for TCB and 2.12 for DMP (44); and, 3.51 for OCT.\*

To determine the equilibrium partition coefficient, subsurface samples were weighed into test tubes with Teflon®-lined caps. Tubes were then filled without headspace with five dilutions of the radio-labeled organic compounds prepared from 0.01M CaCl<sub>2</sub> solution. Four or five replicates were prepared at each concentration at a soil:solution ratio of 1:25 (later modified to 2:25). Tubes were mixed by tumbling for 23 hours at 360 inversions·hr<sup>-1</sup>. Increasing mixing times up to 94 hours produced slight and inconsistent increases in partition coefficient that did not appear to justify the longer contact period. An equivalent set of tubes (controls), with sorbate solutions but without soils, was carried through the test procedure. After mixing, sample tubes were centrifuged at 400-700 rcf for 30 minutes and weighed, and 1 mL subsamples were collected from the supernatant for counting on either a Beckman LS 150 or a Beckman LS 7800 liquid scintillation counter.

Concentrations remaining in the sorbent-solution suspension were compared against mean control concentrations with differences in concentration being translated to mass sorbed. In addition to this difference-based approach, the mass sorbed to the solid phase was measured directly by extraction. After decanting the supernatant and reweighing the tube to

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\*G. Veith, Personal Communication

account for residual solution, the remaining sorbent-solute suspension was shaken for 2 minutes by hand with 15 mL of scintillation cocktail, centrifuged at 400-700 rcf for 20 minutes by hand and the supernatant decanted into scintillation vials. This extraction step was repeated once with the second extract normally contributing 10 percent or less to the total sorbate recovery. Further sequential extraction contributed less than an additional 2 percent. Extraction with dichloromethane, a solvent which Freeman and Cheung (Reference 45) suggest should be more effective in removing sorbate from the organic carbon matrix, did provide a slight increase in the extraction recovery. Handling problems and incompatibility with scintillation counting complicated use of this solvent. The efficiency of sorbent extraction was also checked for selected samples by suspending the sorbent, after two extractions with cocktail, in Cab-O-Sil® and directly counting the residual radioactivity. These measurements indicated no residual sorbate remained with the sorbent. The data obtained from equilibrium batch sorption determinations were fitted to a linear partition equation:

$$x/m = K_p C$$

where  $x/m$  is the mg chemical adsorbed per kg of soil,  $C$  is the concentration in  $\text{mg}\cdot\text{L}^{-1}$  and  $K_p$  is the partition coefficient ( $\text{L}\cdot\text{Kg}^{-1}$ ).

## 2. Results and Discussion

The measured physical and chemical characteristics of the 20 subsurface core samples are presented in Table 7. The method used may not provide accurate results for measured surface areas below  $65 \text{ m}^2\cdot\text{g}^{-1}$ . There is an order-of-magnitude variation in the TOC content over the entire length of the core, but at depths between 290 and 537 cm, the range was small with all values less than 0.2 percent. Clay-sized particle content is poorly correlated with both surface area and CEC. The CEC and surface area are positively correlated (index of determination,  $r^2 = 0.74$ ). Lack of crystalline forms in the clay mineral fraction limited the quantitation of the minerals present in the samples. Available clay mineralogy data show mixed layer illite-montmorillonite clays dominated the clay fraction. Illites generally exhibit a CEC of  $20\text{-}30 \text{ meq}\cdot 100\text{g}^{-1}$  and montmorillonites have CEC values approaching  $100 \text{ meq}\cdot 100\text{g}^{-1}$  (46). Based on the fraction of clays in the subsurface samples and the assumption that only clay is contributing to CEC, illite dominance would yield a CEC value in the range of  $2\text{-}10 \text{ meq}\cdot 100\text{g}^{-1}$ . Samples with measured values exceeding this range probably contain expandable layer clays.

The difference approach and sorbent extraction procedures produced two sets of sorption data from which partition coefficients could be calculated. Ideally, these data sets would be the same and, in samples with relatively high TOC, this is the case. However, a basic problem in determining sorption from solution-phase concentration changes is the lack of precision when sorption is low. In many of these experiments, because of low soil solution ratios less than 15 percent of the compound present in solution was sorbed compared to the 20 to 80 percent of the compound recommended (Reference 47). Variations in equilibrium solution concentrations produced by losses during filling and sampling and sorptive losses to the glass and Teflon® surfaces during the contact period contributed to the imprecision in the solution phase sorption data. The result is that the data



TABLE 7. PHYSICAL AND CHEMICAL CHARACTERISTICS OF SUBSURFACE CORE MATERIALS

Sample No.	Depth to Top of Core (cm)	TOC (%)	Surface Area m <sup>2</sup> ·g <sup>-1</sup>	CEC (meg·100g <sup>-1</sup> )	Ph	Clay (%)	Sand (%)	Silt (%)
1	0	0.48	48.4	7.4	4.9	14	43	43
2	48	0.26	49.6	6.7	4.8	11	43	46
3	69	0.38	75.9	8.7	4.4	17	42	41
4	96	0.27	78.0	8.1	4.8	14	40	46
5	119	0.28	56.8	6.0	4.8	12	52	36
6	145	0.39	79.3	8.8	5.1	13	52	35
7	193	0.89	76.0	11.2	5.4	17	32	51
8	241	0.40	59.1	8.2	5.9	11	45	44
9	262	0.39	63.4	6.1	6.0	13	46	41
10	290	0.19	60.6	8.6	5.9	13	53	34
11	338	0.15	71.7	9.7	6.0	9	53	38
12	409	0.18	83.0	11.4	5.9	6	44	50
13	386	0.17	52.8	8.1	6.1	7	58	35
14	434	0.08	85.8	10.9	6.0	9	34	57
15	483	0.13	95.7	12.1	5.9	13	40	47
16	550	0.14	98.7	11.6	5.8	13	34	53
17	531	0.12	84.3	9.4	5.9	9	46	45
18	579	0.15	95.9	14.0	5.8	12	35	53
19	597	0.23	112.0	23.7	5.7	12	19	69
20	627	0.33	129.1	19.9	5.9	15	40	45

based on solution-phase concentration differences are mostly different from and much less precise than those obtained by sorbent extraction.

Tables 8, 9, and 10 contain partition coefficient ( $K_p$ ), TOC normalized partition coefficient ( $K_{oc}$ ), and index of determination ( $r^2$ ) data for the compounds tested. Experimentation with TCB (Table 8) focused on samples from the upper half of the core. The precision of solution phase sorption data, good in all but Samples 5 and 11, resulted from the greater amounts of sorption from solution because of higher TOC in these samples and the lower solubility (higher  $K_{ow}$ ) of TCB. Figure 7 shows the correlation between  $K_p$ 's and TOC content ( $r^2$  values of 0.63 and 0.73) for solution and extraction phases, respectively. Variations in  $K_p$  are generally accompanied by similar variations, though of differing magnitude, in TOC and clay-sized particle content. The quality of the TCB solution phase results and the similarity between solution and extraction partition coefficient values give the extraction approach some credibility.

Problems with solution-phase interpretation of sorption data are more apparent for OCT (Table 9). Index of determination values suggest the quality of adsorption data obtained by this procedure is suspect. Poor correlation is observed between partition coefficients, calculated from solution phase concentration differences, and both TOC and clay-sized particle content.

TABLE 8. ISOTHERM PARAMETERS FOR 1,2,4-TRICHLOROBENZENE ON  
SELECTED CORE MATERIALS

SOIL	Solution Phase			Extracted Phase		
	$k_p$	$r^2$	$K_{oc}$	$k_p$	$r^2$	$K_{oc}$
1	6.1	0.84	1270	n.a.	n.a.	n.a.
2	3.4	0.80	1310	3.5	1.0	1350
3	4.0	0.96	1050	n.a.	n.a.	n.a.
4	3.1	0.95	1150	2.9	0.98	1070
5	2.8	0.55	1000	2.4	0.97	860
6	7.7	0.95	1970	4.9	0.98	1260
7	11.5	0.97	1290	8.7	0.97	980
8	5.1	0.90	1280	4.0	0.98	1000
9	9.7	0.96	2490	7.6	0.99	1950
10	n.a.	n.a.	n.a.	3.1	0.99	1630
11	1.2	0.49	800	1.8	0.99	1200
20	4.3	0.86	1300	3.8	0.99	1150

All K values are in  $L \cdot kg^{-1}$ ; n.a. indicates analysis not performed.

In contrast, the extraction approach produced reasonable isotherm data with almost all subsurface samples tested including those with low TOC. The  $r^2$  values in Table 9 indicate the improved quality of regressions. The precision of replicates for extracted sorbed mass is considerably better than the solution phase interpretation. Figure 8 shows correlation between OCT  $K_p$  values and TOC content. Index of determination values are 0.29 and 0.82 for solution and extraction data, respectively. Clay-sized particle content is also correlated significantly at the 95 percent confidence level with both partition coefficient and carbon content  $r^2$  values of 0.46 and 0.4, respectively. Other physical and chemical parameters monitored are poorly correlated with partition coefficients.

In deeper samples variations in TOC content were not accompanied by changes in OCT partition coefficients. The index of determination between extraction  $K_p$  and TOC in the lower half of the core (below 290 cm) is 0.27. However,  $K_p$  values for the deeper samples are significantly correlated with clay-sized particle content at the 95 percent confidence level ( $r^2=0.47$ ), although variation on a sample by sample basis with depth is not always consistent. Due to the smaller variation in TOC content in these deeper samples, clay-sized particle content may be a better parameter for describing sorption. More extensive information on clay content and mineralogy might elucidate the partitioning mechanism of OCT in these low TOC samples.

Hassett et al. (Reference 38) noted that the relative contribution of the mineral fractions to total sorption becomes significant as the ratio

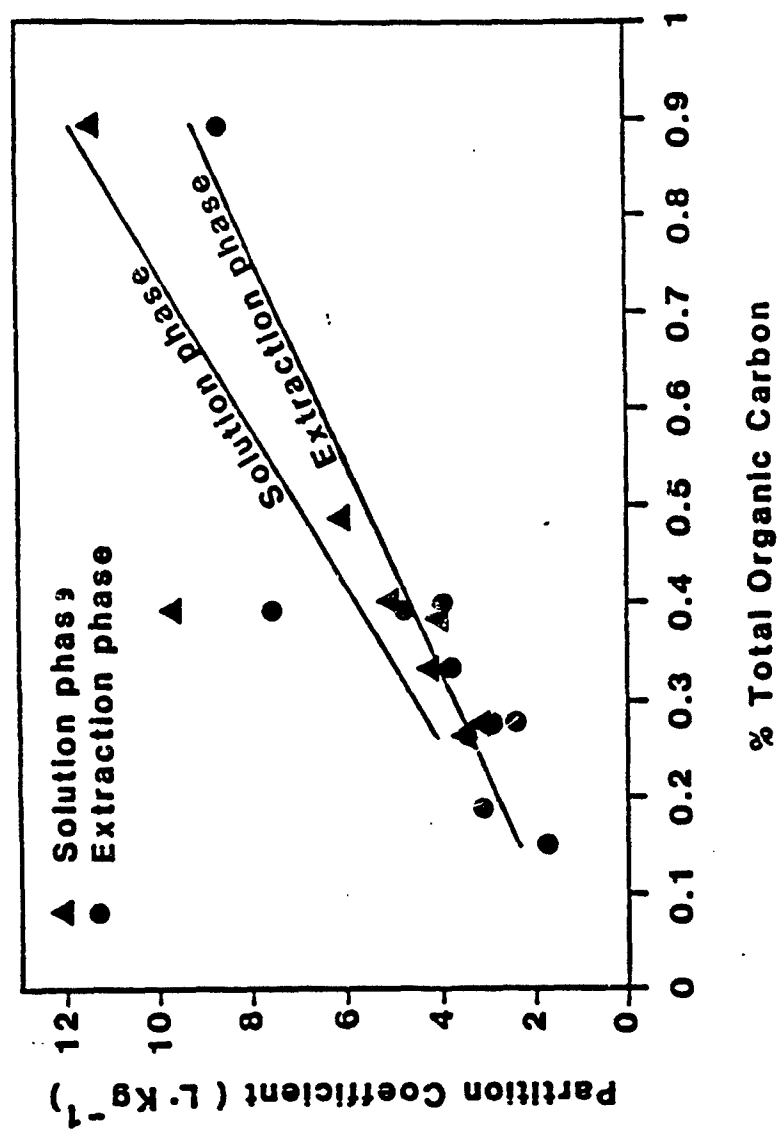


Figure 7. Correlation of Solution- and Extraction-Phase Sorption of 1,2,4-Trichlorobenzene with Total Organic Carbon of Core Materials.

TABLE 9. ISOTHERM PARAMETERS FOR O-CHLOROTOLUENE ON SUBSURFACE CORE MATERIALS

Soil	Solution Phase			Extracted Phase		
	K <sub>p</sub>	r <sup>2</sup>	K <sub>oc</sub>	K <sub>p</sub>	r <sup>2</sup>	K <sub>oc</sub>
1	1.8	0.77	380	1.4	0.99	290
3	1.0	0.74	260	1.3	0.98	340
4	2.7	0.74	1000	0.9	0.99	330
5	2.3	0.75	820	0.9	0.99	320
6	1.7	0.80	440	2.0	0.99	510
7	3.7	0.92	420	2.6	0.99	290
8	0.5	0.57	120	1.3	0.92	320
9	1.1	0.49	280	1.6	0.99	410
10	1.3	0.82	680	1.0	0.99	530
11	0.7	0.57	470	0.4	0.98	270
12	1.6	0.93	890	0.3	0.96	170
13	1.0	0.88	590	0.3	0.87	180
14	1.4	0.60	1750	0.7	0.98	880
15	0.5	0.71	380	0.3	0.94	230
16	1.8	0.66	1290	0.6	0.99	430
17	1.5	0.86	1250	0.5	0.99	420
18	2.0	0.67	1330	0.7	0.98	470
19	1.5	0.59	650	0.8	0.90	350
20	2.6	0.90	790	1.0	0.98	300

All K values are in L·kg<sup>-1</sup>.

of swelling clay to organic carbon increases. Karickhoff (Reference 39) observed a ratio threshold value of >60 (clay minerals/TOC) for mineral surfaces to make a discernable contribution to sorption of nonpolar organics with the ratio decreasing to 25-60 for compounds with polar functional groups. In Figure 9, K<sub>oc</sub> values for OCT are plotted against the ratio of total clay minerals to TOC. For clay/TOC greater than 60, mineral contribution was indicated. With illite dominating the clay content in most of the samples the threshold value observed is consistent with other findings (References 38, 39).

Selected subsurface samples were tested for sorption of DMP to evaluate the degree of sorption of a compound with more polar character. Results of sorption isotherms and calculated K<sub>oc</sub> values appear in Table 10. The effect of varying soil solution ratio was evaluated for Sample 6 by performing concurrent isotherm experiments at three different ratios. For this sorbent, the threefold variation in K<sub>oc</sub> values for these three ratios further signifies the unreliability of estimating sorption in this system from the solution phase data. Extraction phase results indicate a slight but consistent increase in K<sub>p</sub> with increasing amount of soil.

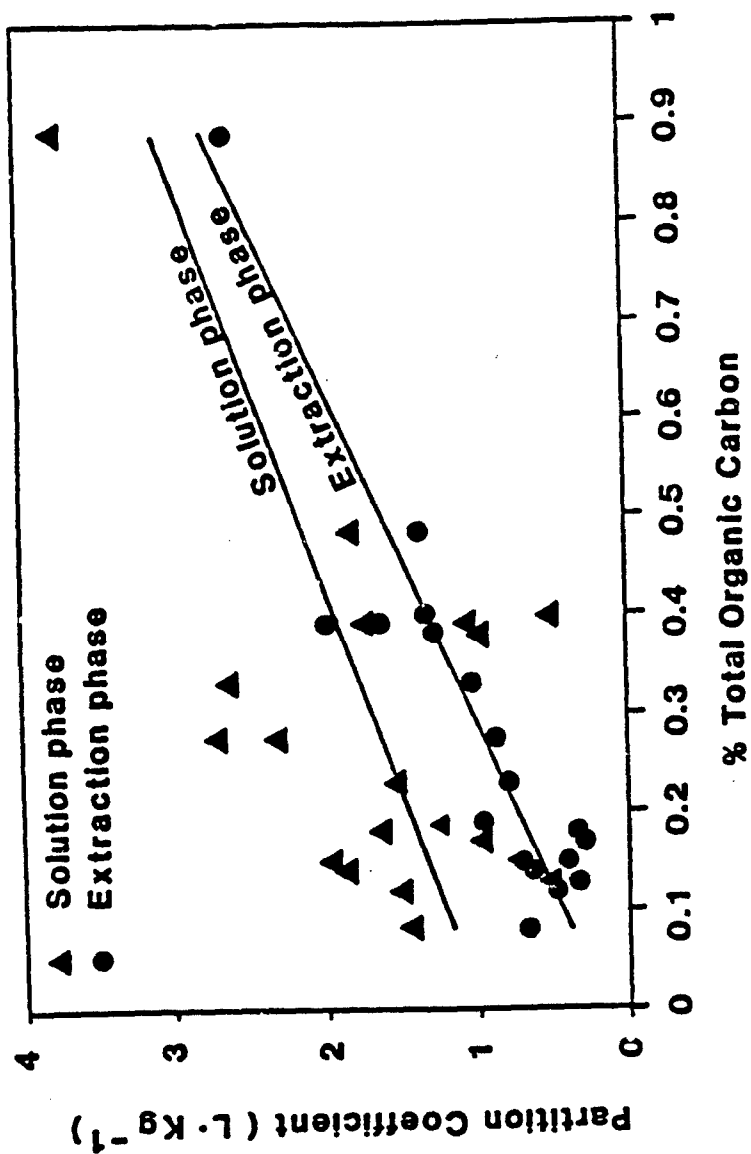


Figure 8. Correlation of Solution- and Extraction-Phase Sorption of o-Chlorotoluene with Total Organic Carbon of Core Materials.

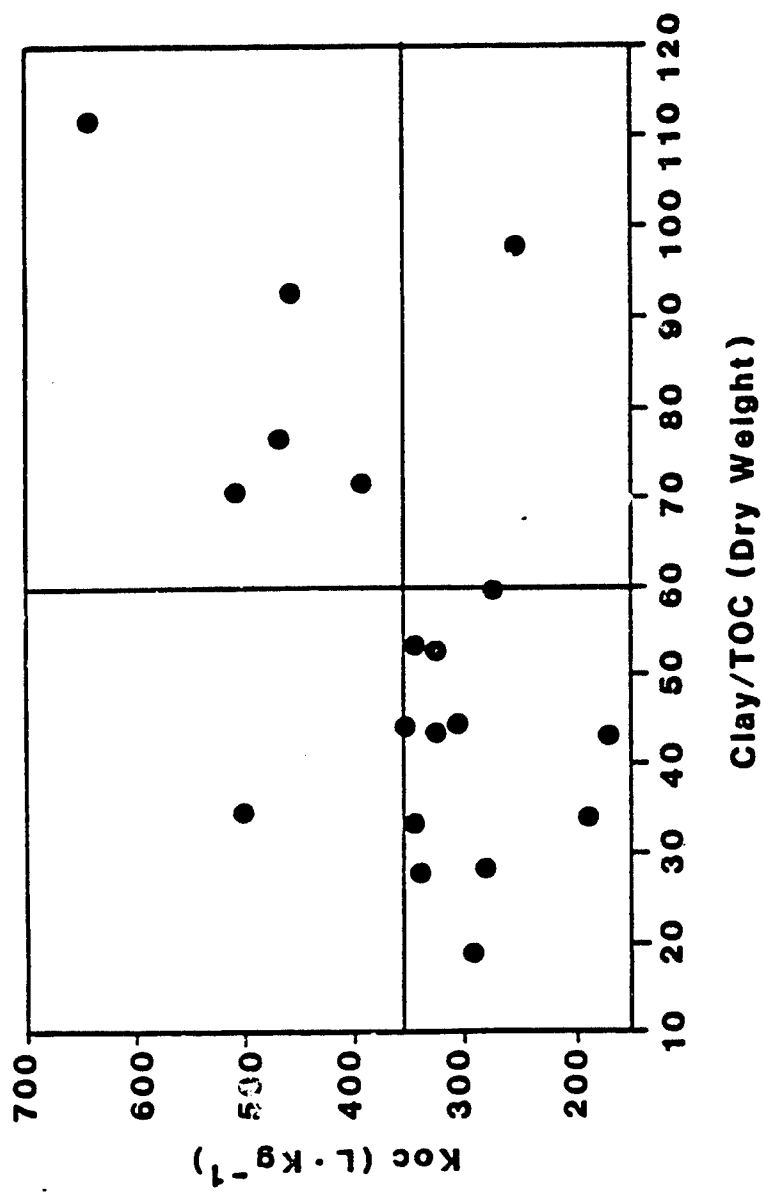


Figure 9. Influence of Total Clay Content of Core Material on Sorption of o-Chlorotoluene.

TABLE 10. ISOTHERM PARAMETERS FOR DIMETHYLPHTHALATE ON SELECTED CORE MATERIALS

Soil	Solution Phase			Extracted Phase		
	K <sub>p</sub>	r <sup>2</sup>	K <sub>oc</sub>	K <sub>p</sub>	r <sup>2</sup>	K <sub>oc</sub>
1	0.7	0.46	150	0.4	0.87	80
6(1:5)*	2.1	0.99	540	1.4	1.00	360
6(1:10)	2.8	0.97	720	1.2	1.00	310
6(1:25)	6.2	0.89	1590	1.2	1.00	310
7	2.1	0.89	240	1.5	0.99	170

\*All K values are in L·kg<sup>-1</sup>. Numbers in parentheses are solids solution ratios.

The K<sub>oc</sub> values for the three sorbates generally reflect differences in their octanol-water partitioning. For TCB, the mean K<sub>oc</sub> values ( $\pm 1$  standard deviation) obtained for the solution ( $1460 \pm 440$ ) and extraction ( $1240 \pm 310$ ) approaches were similar. The OCT solution phase K<sub>oc</sub> values (mean value of  $730 \pm 20$ ) vary over an order of magnitude while extraction values are within a factor of 5, with a mean of  $370 \pm 150$ . The mean extraction phase K<sub>oc</sub> value obtained for DMP on three sorbents was  $190 \pm 120$ .

In Figure 10, extraction phase distribution coefficients measured in this study are compared with those predicted from two literature K<sub>ow</sub>-K<sub>oc</sub> relationships on a log-log plot. Correlation between log K<sub>oc</sub> and log K<sub>ow</sub> for TCB and OCT shows sorption considerably below that predicted by Schwarzenbach and Westall (Reference 35) but roughly equivalent to that observed by Briggs (Reference 34). The elevated K<sub>oc</sub> value for DMP suggests a greater sorption contribution from noncarbon surfaces than for the other sorbates. The better agreement between results from this study and Briggs' regression equation is due partly but not entirely to the similar ranges of K<sub>ow</sub> values for the sorbates tested in the two studies. Schwarzenbach and Westall (Reference 35) found a mean log K<sub>oc</sub> value for TCB of 3.52, a value outside the range observed here. Differences in the effectiveness of the carbon to sorb organic molecules, observed for binding of organics by surface water dissolved organic carbon (Reference 48), may contribute to an explanation of the K<sub>oc</sub> variations. Carbon associated with deeper geologic strata is older and has been exposed to more intensive and varied diagenetic and microbial alteration. Further, the carbon may be distributed differently in this environment, perhaps in more widely dispersed patches or in thinner films that would make it less available to the sorbate or less able to compete with other sorbing surfaces.

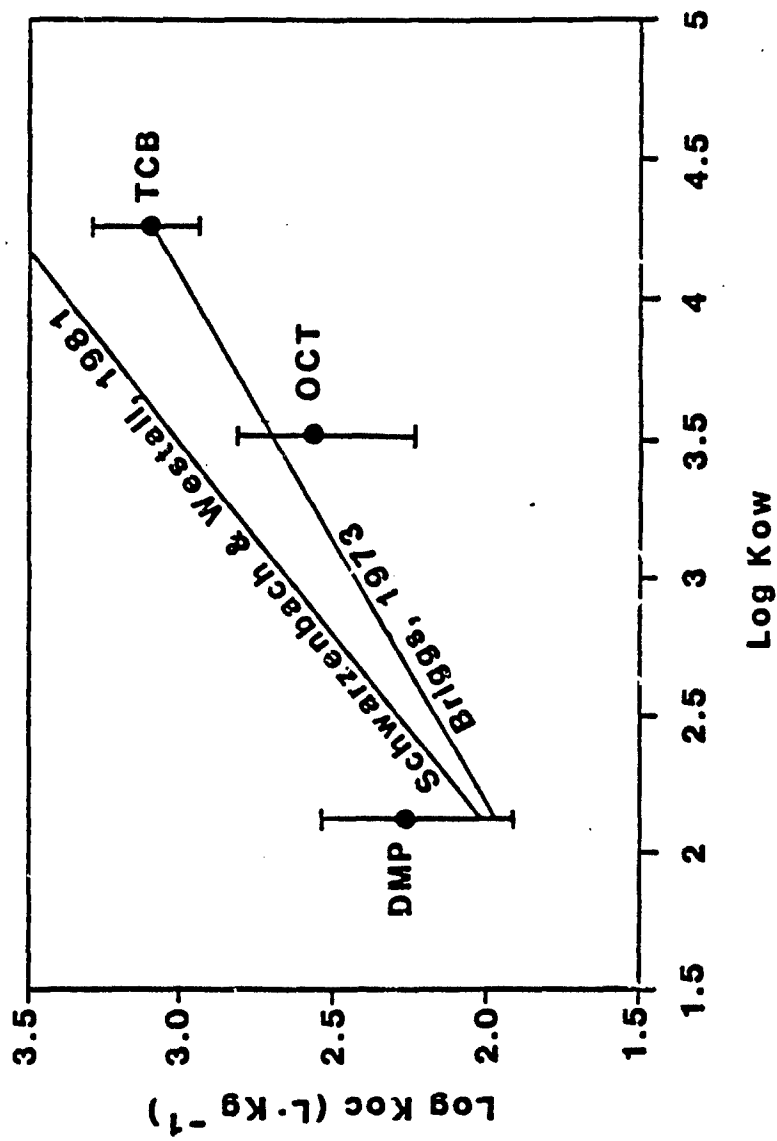


Figure 10. Comparison of Observed Koc-Kow Data with Selected Regressions (References 34 and 35).



At the soil:solution ratio used in this study, colloidal sorbent would be expected to contribute to the solution phase concentration of sorbate. Research by Voice et al. (Reference 49) has shown that partition coefficients were strongly and inversely influenced by sorbent concentration. This phenomenon is further described in terms of sorbent contributions to the solution phase that are not readily separated by conventional methods, e.g., centrifugation. These nonseparated high organic carbon particulates, contributed to the solution phase as a direct function of solids content of the reaction mixture, were found to significantly affect the partition coefficient for chlorinated biphenyls (Reference 50). While this phenomenon occurred in the studies presented here, the impact on the observed results should be minimized because of three factors: (1) soil:solution ratios were low; (2) TOC content was relatively low in many of these sorbents; and, (3) the sorbates used were of low to medium hydrophobicity.

The data developed in this study show that determination of the sorption of compounds of low to moderate hydrophobicity on subsurface solids of low sorptive capacity is best achieved by extracting and measuring the quantity of compound actually sorbed on the solid phase rather than measuring solution phase concentration differences. This approach provides a much more precise determination of  $K_p$ , especially if solids solution ratios are kept low to minimize effects of sorption by colloid sorbents which may be contributed to the solution phase by the solids. By selecting the appropriate volumes for the reaction vessel and the extractant, it is possible to do the extraction directly in the reaction vessel and to use all the recovered extractant for scintillation counting, minimizing handling and improving precision.

Sorption isotherm data for the sorbates evaluated, based on sorbate extraction from the solid phase after appropriate solution phase contact, suggest that, in subsurface samples, sorbent TOC content is a reasonably good predictor of sorption down to about 0.2 percent TOC, in reasonable agreement with the conclusions of Schwarzenbach and Westall (Reference 35). However, as the  $K_{oc}$  values decline with the decrease in hydrophobicity of the sorbates, the imprecision of the  $K_{oc}$  estimate (measured in terms of relative standard deviation) increases appreciably, demonstrating an interrelationship between sorbate properties and sorbent characteristics other than TOC. For DMP, the observed  $K_{oc}$  value exceeds the values predicted by various empirical relationships from the literature. That clay content, in some form, may be an important predictor of sorption is indicated by the OCT sorption data when total clay:TOC ratio exceeds 60.

It appears that for very hydrophobic molecules, TOC content of the sorbent will control sorption down to levels of organic carbon that defy quantitation. Conversely, sorption of less hydrophobic organics will likely be affected by clay mineral surfaces, amorphous metal oxides and perhaps other characteristics in many unsaturated and most saturated subsurface environments where organic carbon content is quite low. The magnitude, nature, and kinetics of these processes for a variety of slightly polar to ionic organic contaminants must be developed before their subsurface transport can be understood. These efforts, to a large degree, depend on accurate

measurement, often at low levels, of subsurface parameters including clay content and mineralogy, surface area, and TOC.

The nature and distribution of the organic carbon in the deeper subsurface also require investigation. The results presented here suggest that carbon associated with low TOC subsurface sorbents may be less efficient in hydrophobically bonding organic contaminant molecules than many of the surface soils and sediments examined in other studies.

## B. SORPTION OF VOLATILE ORGANIC COMPOUNDS ON SELECTED SUBSURFACE SOLIDS

Volatile organic compounds of low polarity, including chlorinated hydrocarbon solvents and many aromatic petroleum hydrocarbons, have relatively high water solubilities and, consequently, low octanol-water partition coefficients (Kow's). Hence, these compounds usually are not strongly sorbed in soils and sediments, which contributes significantly to their frequent appearance as ground water pollutants. On a relative basis the extent of sorption of such volatile organic contaminants in aquifer systems will be less than in the higher carbon soils and sediments; nevertheless, interactions between these molecules and the mineral surfaces of aquifer solids may be important. Over long times and distances, even a small retardation factor will contribute to the size of a pollutant plume (Reference 51) and cause a substantial increase in the volume of water that must be pumped and treated to realize aquifer remediation.

Not much attention has been given to sorption of volatile organic molecules to aquifer material. Curtis et al. (Reference 52) measured sorption of tetrachloroethene (PCE), 1,2-dichlorobenzene (DCB) and other solvents on Borden aquifer material and found sorption in excess of what would be expected based on TOC. Curtis and Roberts (Reference 53) have shown that the sorption interactions were not due solely to aqueous phase activity of the solutes and suggests that mineral surfaces play an important role in the sorption process in that aquifer material.

The research described below involved evaluation of the sorption of several volatile organic compounds of low polarity on selected subsurface materials. The overall objectives were to describe sorption of the test compounds on these low TOC sorbents and attempt to define a mineral component to that sorption, thus, providing information needed for developing more effective aquifer remediation strategies. The study was conducted in two phases. The first phase focused on the sorption of PCE on solids from two semicontinuous subsurface cores. The second phase examined sorption of four nonpolar volatile organic compounds on four low-TOC aquifer materials.

### 1. Materials and Methods

#### a. Acquisition and Characterization of Subsurface Materials

The subsurface solids used in this study were, with one exception, collected near Lula, Oklahoma, using a rotary drilling rig with coring capabilities. Most of the materials were obtained from two depth

cores designated herein as the J and N cores. The J core was the same core that provided the subsurface solids used in the earlier sorption study described in Subsection III A. This core consisted of 20 contiguous sections down to a depth of 675 cm, as described previously in Table 7. The N core samples were obtained at approximately 90 cm intervals down to a depth of 600 cm and included two samples of saturated zone material. In addition to these J and N core materials, another aquifer material sample from the Lula area was prepared by compositing a series of saturated zone samples collected from a group of boreholes drilled at this site. This material was designated C-1. Finally, a sample of aquifer material from the Canadian Forces Base at Borden, Ontario, Canada, was provided by Stanford University personnel. This material was designated B-1.

The procedures employed for acquisition and characterization of the aquifer materials were essentially the same as those employed in the earlier sorption study, as described in, Section III A.1.a.

b. Determination of Partition Coefficients and Sorption Isotherms.

Four volatile organic compounds of low polarity, namely benzene (Bz), trichloroethylene (TCE), tetrachloroethylene (PCE), and dichlorobenzene (DCB), were employed in this study. These compounds were obtained labeled with  $^{14}\text{C}$  from Pathfinders Laboratories, Inc., St. Louis, Missouri.

During the first phase of the study, partition coefficients were determined by essentially the same procedure as those employed in the earlier sorption study, as described in, Section III A.1.a. A minor modification involved prewetting soils with 0.01M  $\text{CaCl}_2$  to displace trapped air.

In Phase 2, the sorbents were ground and sieved to pass through either a 250 or 500  $\mu\text{m}$  sieve. Sorbents were split, first with a Soiltest splitter and then by serial splitting on a Quantachrome riffle splitter down to a desired mass that was transferred directly into the reaction tube. The mean mass transferred to the 24 tubes of an isotherm series routinely showed a relative standard deviation of 1.5 percent or less. The splitting procedure insured that each tube contained a reproducible solid sample representative of the bulk material.

Another procedural change implemented in Phase 2 of the study involved introduction of the sorbate into the tubes. To improve the precision of addition, especially with the very volatile sorbates, additions were made from a methanol stock with a 5 or 10  $\mu\text{L}$  syringe to tubes containing solid samples and filled with 0.01M  $\text{CaCl}_2$  solution. Tubes were sealed with Teflon<sup>®</sup>-lined septa screw caps immediately after the addition. The tube to tube variability inherent in reproducing a syringe delivery volume was less than that introduced by volatilization from the aqueous phase transfer procedure used in Phase 1. Methanol concentrations in the tubes never exceeded 0.1 percent by volume, so produced no measurable effect on sorbate aqueous phase activity (Reference 54).

After mixing the tubes for 21-24 hours, samples were centrifuged at 4000 r/min for 1 hour in a Sorvall® RC-2 centrifuge fitted with an SM-24 rotor. The subsequent steps of decanting, extracting and counting were similar to those used in Phase 1. However, the second extraction was continued overnight (~20 hours) after preliminary tests indicated slightly higher recoveries could be obtained with this modification.

Sorption data were calculated from the total mass of sorbate recovered from the sorbent by extraction, corrected for pore water remaining after decanting. Isotherm partition coefficients were obtained for linear and Freundlich interpretations from equations (1) and (2).

$$S = K_p C \quad (1)$$

where S is the mass of chemical sorbed per mass sorbent ( $\text{mg} \cdot \text{kg}^{-1}$ );  $K_p$  is the partition coefficient determined from extraction of the solid phase in ( $\text{L} \cdot \text{kg}^{-1}$ ); and C is the equilibrium solution concentration ( $\text{mg} \cdot \text{L}^{-1}$ ).

$$S = K_f C^{1/n} \quad (2)$$

where  $K_f$  is the Freundlich coefficient and  $1/n$  is an empirical fitting parameter indicative of the deviation of the data from linearity.

## 2. Results and Discussion

### a. Equilibration Time

Questions concerning the time required to attain sorption equilibrium were addressed by conducting experiments with PCE on J-1 and with DCB on N-1. Curtis and Roberts (Reference 53) reported that, on B-1 aquifer material, PCE and DCB approached equilibrium over about 3 days. Their data showed that roughly 90 percent of the ultimate sorption was reached in 24 hours and that the losses from the blanks made data interpretation more difficult as contact times were increased. In this study the functional working range for mixing time was found to actually be some compromise between attaining sorption equilibrium and losing sorbate from the test system through volatilization or other processes. The statistical estimate of partition coefficients became progressively worse at longer contact times, reflected in increasing 95 percent confidence intervals around the partition coefficient estimates. The PCE data suggested that 12 hours of mixing yielded a reasonable estimate of  $K_p$  while the data for DCB showed that the distribution coefficient continued to slowly increase to 48 hours but became statistically indistinguishable at 24 hours. Therefore, a 21-24 hours mixing time was used in all batch tests, yielding data of acceptable statistical precision that were amenable to comparison.

### b. Isotherm Linearity

Most Phase 1 isotherms were determined on J and N core materials. The pertinent characteristics of the N core samples are presented in Table 11, while the J core materials have previously been described in detail in Table 7.

TABLE 11. PERTINENT CHARACTERISTICS OF N CORE SAMPLES

Sample No.	TOC (%)	Clay-size fraction (%)
N-1	1.33±0.11	12.8
N-2	0.054±0.002	24.0
N-3	0.039±0.003	20.8
N-5	0.034±0.002	34.0
N-6	0.028±0.007	14.5
N-7	0.042±0.004	11.6

Data are from air-dried and ground samples sieved through a 1 mm sieve. TOC mean and standard deviation are based on triplicate analysis. Clay data are means for 4-6 replicates.

The solution concentration range selected in Phase 1 for many of the PCE isotherms includes concentrations (12-15 mg·L<sup>-1</sup>) well above the limits suggested by Karickhoff (Reference 55). The higher solution concentrations used in generating these isotherms are not uncommon in contaminated ground water situations. The data show definite trends to nonlinearity at higher equilibrium concentrations. In Table 12, isotherm parameter values are presented for the complete data sets, and for the isotherms (slopes designated  $K_3$ ) after the highest concentration points are eliminated. In a representative isotherm, five replicate sorption tubes were prepared at each concentration level, so that eliminating a concentration level eliminates five replicate data points. Sorption data for equilibrium concentrations at or below 2 mg·L<sup>-1</sup> were forced through zero to yield the  $K_0$  values in Table 12. Finally, Table 12 contains Freundlich coefficients,  $K_f$ , for the complete data sets.

Comparison of the  $K_p$ ,  $K_3$ , and  $K_0$  data shows increasing intercepts and decreasing slopes indicative of nonlinearity as higher equilibrium concentrations are incorporated into the isotherm regression. Further,  $K_f$  and  $K_0$  values are nearly identical in all cases.

Sorption isotherm data in which the highest equilibrium PCE concentrations did not exceed 2 mg·L<sup>-1</sup> are presented in Table 13. Partition coefficient values for the linear and Freundlich interpretations of the data are nearly equivalent. The linear regression intercepts are small positive values and the  $1/n$  values are greater than 0.9 throughout. These data show that sorption of PCE to subsurface sediments can be linearly expressed for equilibrium concentrations to about 2 mg·L<sup>-1</sup>.

TABLE 12. PARTITION COEFFICIENT VALUES FOR PCE SORPTION FROM HIGH-CONCENTRATION SOLUTIONS

Soil	$K_f$	1/n	$r^2$	$K_p$	B	$r^2$	$K_3$	B	$r^2$	$K_0$
N-5	0.26	0.95	0.94	0.25	-0.03	0.89	0.19	0.08	0.77	0.28
N-7	0.46	0.92	1.00	0.37	0.07	0.99	0.38	0.06	0.98	0.44
J-6	0.58	0.88	1.00	0.41	0.20	1.00	0.46	0.12	1.00	0.59
J-7	1.60	0.89	0.99	1.14	0.63	0.99	1.40	0.17	0.97	1.53
J-9	0.98	0.89	1.00	0.69	0.41	0.99	0.84	0.13	1.00	0.99
J-11	0.60	0.81	0.98	0.35	0.26	0.97	0.39	0.19	0.91	0.61
J-12	0.50	0.81	0.98	0.29	0.24	0.94	0.34	0.15	0.95	0.53
J-14	1.74	0.93	1.00	1.48	0.19	1.00	1.55	0.11	0.98	1.68

B represents the regression line intercept. For  $K_0$  the intercept was, by definition, zero. All K values except  $K_f$  are in  $L \cdot kg^{-1}$ .

TABLE 13. SORPTION OF PCE FROM LOW CONCENTRATION AQUEOUS SOLUTIONS BY SUBSURFACE MATERIALS

Soil	Size ( $<X$ mm)	$K_f$	1/n	$r^2$	$K_p$ ( $L \cdot kg^{-1}$ )	B	$r^2$
N-1	1	2.93	0.96	1.00	2.98	0.02	1.00
N-2	1	0.32	0.93	0.98	0.34	$<0.01$	0.97
N-3	1	0.31	0.94	0.99	0.31	$<0.01$	0.98
N-6	0.25	0.19	0.99	0.99	0.18	$<0.01$	0.98
J-10	0.25	0.48	0.94	0.99	0.48	$<0.01$	0.99
J-19	1	0.37	0.97	0.99	0.37	$<0.01$	0.99
B-1	0.5	0.35	0.93	1.00	0.35	$<0.01$	0.99
C-1	0.5	0.20	0.95	0.98	0.19	$<0.01$	0.97

### c. Mineral Phase Sorption

The relationship between sorption of PCE and sorbent TOC was also investigated in Phase 1. Best estimates of the partition coefficient for the linear portion of the isotherm for those sediments with TOC greater than 0.1 percent are plotted as Figure 11. There is a strong correlation

between PCE sorption and TOC for these subsurface samples. Linear regression of the data yields the following empirical relationship:

$$K_p = 2.00 (\text{TOC}) + 0.06 \quad (r^2 = 0.95) \quad (3)$$

where TOC is expressed as percent. This relationship expresses the magnitude of partitioning of PCE into the natural organic matter of these sorbents as measured in the experimental system employed in this study. It follows that, using this relationship, the partition coefficients for PCE on other subsurface samples can be predicted within some modest error bounds.

In Phase 2, the hypothesis that sorption of PCE and related nonpolar organic solvents occurs on aquifer materials in excess of normal anticipation, based on the TOC contents of the solids, was tested. Four subsurface samples were selected as sorbents, and four volatile organic compounds were chosen as sorbates. Three of the solids were low TOC aquifer materials while the fourth was from the unsaturated zone J core used in Phase 1. The intent was to determine the magnitude of the carbon-based sorption of each of the sorbates on the higher TOC J core sample, and to use this data to predict the magnitude of the carbon-based sorption on the low TOC aquifer material. Any sorption in excess of that predicted would then be attributed to mineral surface interactions.

Some characteristics of the subsurface samples, including total surface area (TSA) and cation exchange capacity (CEC), are given in Table 14. The aquifer samples, B-1, C-1, and N-6, had TOC levels well below the 0.1 percent minimum proposed by Schwarzenbach and Westall (Reference 35), while the unsaturated zone sample, J-10, was estimated to have sufficient carbon to control sorption of all the sorbates. CEC and TSA were quite low in all the samples and did not show appreciable variation.

TABLE 14. CHARACTERISTICS OF AQUIFER SOLIDS

Sample	Size Fraction ( $\mu\text{m}$ )	TOC (%)	Clay-size Fraction (%)	TSA ( $\text{m}^2 \cdot \text{g}^{-1}$ )	CEC ( $\text{meq-NH}_4^+ \cdot \text{g}^{-1}$ )
B-1	<500	0.031 $\pm$ 0.001	11.0	<10	1.5 $\pm$ 0.3
C-1	<500	0.021 $\pm$ 0.004	14.0	11 $\pm$ 1.2	2.5 $\pm$ 0.2
N-6	<250	0.028 $\pm$ 0.002	23.0	30 $\pm$ 2.0	4.5 $\pm$ 0.4
J-10	<250	0.26 $\pm$ 0.01	13.5	46 $\pm$ 3.2	7.2 $\pm$ 0.4

$\pm$  values signify one standard deviation about the mean usually based on three replicates.

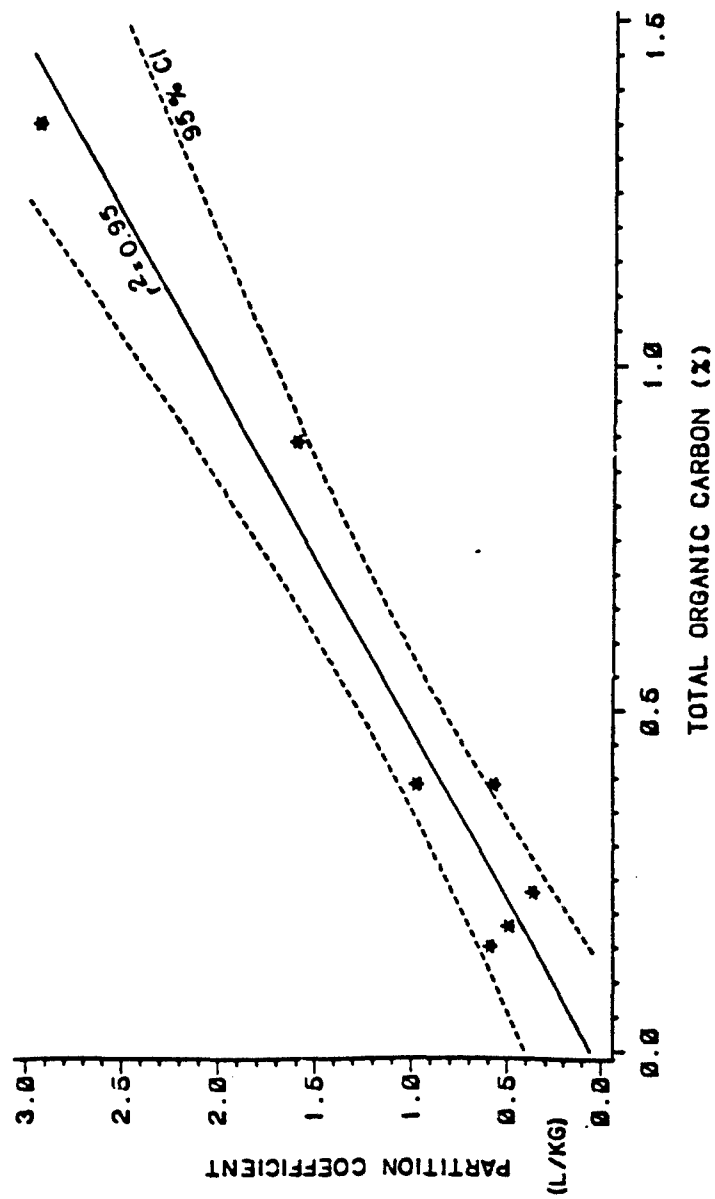


Figure 11. Tetrachloroethylene Sorption Dependency on Sorbent Organic Carbon Content.



Measured  $K_p$  values for the various compounds and subsurface materials are presented in Table 15. The 95 percent confidence intervals for the  $K_p$  estimate within any isotherm experiment are narrow, and generally improve as the sorbate volatility decreases and the sorbent TOC increases. Replicate isotherms for DCB on J-10 show reproducibility of the  $K_p$  estimate to within 80 percent. The  $K_p$  value for PCE sorption on J-10 sorbent compares favorably with the value of 0.58 predicted from Equation (3) and the measured TOC of the sorbent, supporting the contention that this sorbent has sufficient TOC to control the sorption of these nonpolar organics.

TABLE 15. MEASURED PARTITION COEFFICIENTS FOR VOLATILE ORGANIC COMPOUNDS ON AQUIFER MATERIALS

Sorbent/Solvent		BZ	TCE	PCE	DCB
Log $K_{ow}$		2.1	2.3	2.9	3.4
B-1	$K_p$	0.038	0.088	0.35	0.34
	CI	0.030-0.045	0.076-0.098	0.33-0.37	0.31-0.37
	$r^2$	0.859	0.940	0.992	0.969
C-1	$K_p$	0.026	0.032	0.19	0.82
	CI	0.021-0.031	0.029-0.036	0.17-0.21	0.072-0.091
	$r^2$	0.886	0.952	0.975	0.948
N-6	$K_p$	0.035	0.076	0.18	0.23
	CI	0.031-0.039	0.069-0.083	0.17-0.19	0.22-0.24
	$r^2$	0.951	0.965	0.985	0.997
J-10	$K_p$	0.12	0.16	0.48	1.04
	CI	0.11-0.13	0.15-0.18	0.45-0.50	1.01-1.08
	$r^2$	0.973	0.966	0.990	0.995
	$K_p$				0.85
	CI				0.82-0.89
	$r^2$				0.994

The table includes data on the 95 percent confidence interval (CI) and regression coefficient ( $r^2$ ) for each partition coefficient. A repeat isotherm was performed with DCB on sorbent J-10. Log  $K_{ow}$  values are from Callahan et al. (Reference 44)

Further evaluation of this point can be made by examining the relationship between sorption and the octanol-water partition coefficients of the sorbates. This is commonly done by normalizing the  $K_p$  values to the sorbent TOC, as in Equation (4), then plotting the log of the normalized  $K_p$ , designated  $K_{oc}$ , against log  $K_{ow}$ .

$$K_{oc} = K_p / f_{oc} \quad (4)$$

where  $f_{oc}$  is the mass fraction of carbon in the sorbent. Such a plot of J-10 data is presented in Figure 12. Schwarzenbach and Westall (Reference 35), as well as numerous other researchers, have presented similar data for sorption of a variety of nonpolar organic compounds on numerous soils, sediments, and sludges. The data obtained in this study are compared with that of Schwarzen-

bach and Westall (SW) because they worked with similar sorbates and sorbents under similar testing conditions. Data obtained in the previous sorption study described in Subsection III A above were consistent with SW, but about a factor of two lower.

The SW regression line is also plotted in Figure 12. Data for J-10 falls parallel to and about a factor of 2 below the SW line. These data indicate that carbon is, in fact, controlling sorption of these sorbates on this sorbent. The regression line Equation (5) generated from the J-10 data can now be used to predict the extent of carbon-based sorption on the other sorbents.

$$\text{Log } K_{oc} = 0.69 \text{ Log } K_{ow} + 0.22 \quad (r^2=0.99) \quad (5)$$

Use of  $K_{oc}$  generally implies that the sorbent TOC adequately accounts for the observed sorption. No such assumption was made when the aquifer material sorption data were plotted in Figure 12.  $K_{oc}$  does, however, serve as a useful concept in demonstrating the differences in sorption between the aquifer materials and J-10 sorbent. If TOC were controlling sorption on these aquifer samples, the data points should be co-linear with the J-10 regression line. Instead, data for each of the sorbates except DCB are well above the SW regression line. The implication is that mechanisms other than partitioning into sorbent TOC are important in sorption of nonpolar organics in many saturated systems. The disparity of the DCB data may reflect kinetic limitations of this bulkier molecule.

A crude attempt was made to estimate the relative importance of the mineral contribution to sorption on the aquifer materials used in this study. The amount of sorption expected for these materials, based on their TOC contents and the  $K_{ow}$  of the sorbates, was calculated from Equation (5) above. Then the portion of  $K_p$  attributable to the mineral fraction was calculated on the assumption that  $K_p$  is the result of the sum of its components, as indicated below.

$$K_p = K_{\text{carbon}} + K_{\text{mineral}} \quad (6)$$

$K_{\text{mineral}}$  values were then divided by  $K_p$ 's, and these ratios are presented in Table 16.

While by no means conclusive, the data indicate that sorption attributable to hydrophobic partitioning to the solid phase carbon does not explain a substantial portion (60-80 percent) of the sorption observed. There appears to be no correlation between the sorption observed on the various sorbents and those general parameters representative of the mineral components, such as clay content or TSA. The ranges observed for these characteristics may not have been sufficient to give such clear correlations.

The chlorinated ethenes do seem to exhibit slightly more noncarbon sorption (70-80 percent) than do the aromatics (60 percent). The

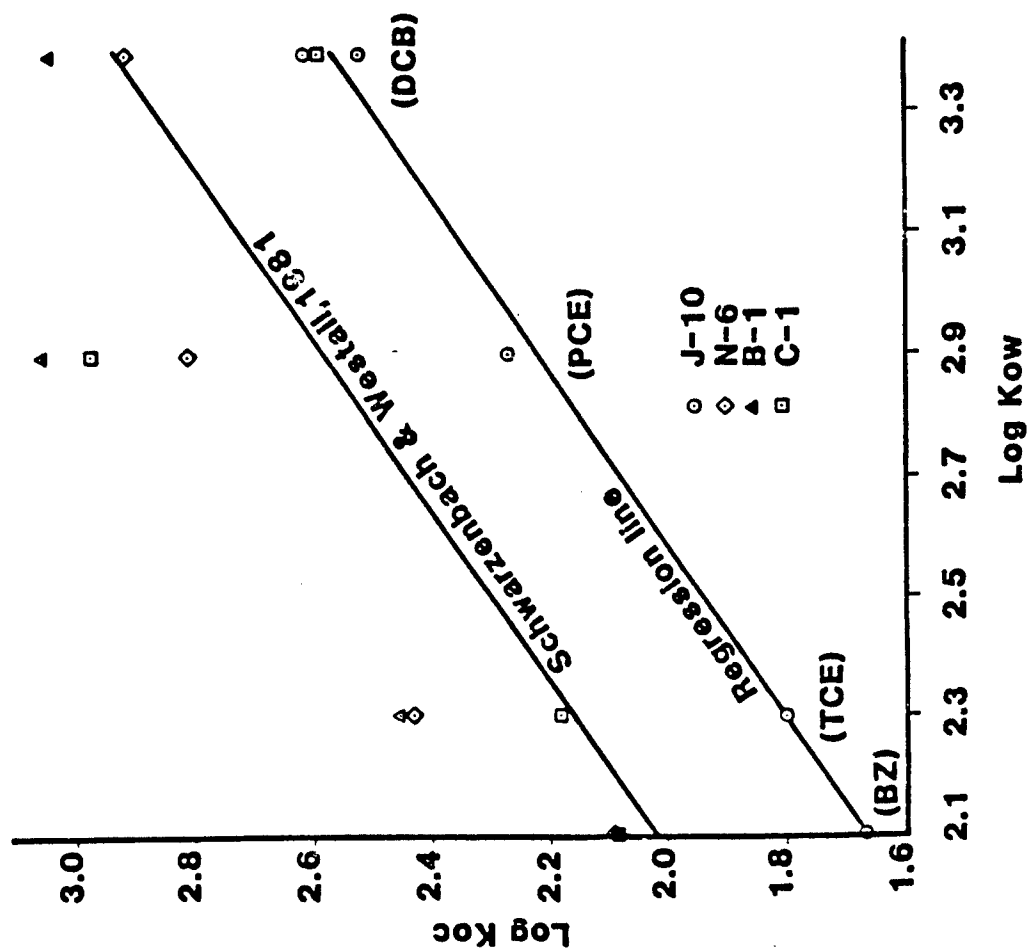


Figure 12. Carbon-Normalized Sorption of Volatile Organic Molecules on Subsurface Sediments.

TABLE 16. FRACTION OF SORPTION ATTRIBUTABLE TO MINERAL INTERACTIONS

Aquifer Material	B-1	C-1	N-6
Compound			
BZ	0.6	0.6	0.6
TCE	0.8	0.6	0.8
PCE	0.8	0.8	0.7
DCB	0.7	0.1	0.6

general trend in the aquifer material sorption data in Figure 12 is to increasing sorption with increasing sorbate  $K_{ow}$  at approximately the same slope observed for the carbon-based sorption on sorbent J-10. Whether this implies solution-driven processes where sorption is proportional to aqueous phase activity, or a relatively constant mineral contribution on top of the entropy-driven carbon component cannot be delineated in this effort. This observation cannot be extended to higher  $K_{ow}$  organic compounds until information on the sorptive behavior of these compounds on aquifer materials becomes available.

It is useful to examine the environmental significance of this sorption data. Retardation of pollutant movement in the subsurface is defined as:

$$R = V_w/V_p = 1 + K_p(\rho/\theta) \quad (7)$$

where  $R$  is the retardation of the pollutant relative to water;  $V_p$  and  $V_w$  are the velocities of the pollutant and water, respectively;  $\rho$  is the bulk density of the matrix; and  $\theta$  is the volumetric water content of the matrix, equivalent to the porosity in saturated media. Assuming that representative values for  $\rho$  and  $\theta$  are 1.6 and 0.4, respectively, a  $K_p$  value of 0.25 would be required to generate  $R = 2$ , the condition where the mass of pollutant is equally distributed between the aqueous and solid phases. In light of limitations on water velocity determinations in the field, contaminants with  $R$  values less than 2 can be considered as moving with the water. From the data in Table 15, benzene and trichloroethene would fall into this category in many low carbon aquifers.

The results of this study clearly show that sorption of non-polar volatile organic compounds onto aquifer materials from aqueous solution occurs to a greater extent than would be predicted from a carbon-controlled model of the system. There seems little doubt that this is the result of sorption of the organic compounds onto mineral surface of the aquifer solids. Until further predictive capabilities that account for mineral surface sorption are developed, it will probably be necessary to do site-specific sorption experiments before transport of nonpolar, as well as polar, organic pollutants in low-carbon aquifers can be completely defined.

Even considering the mineral contribution, sorption of some volatile organic contaminants such as B<sub>2</sub> and TCE in very low carbon subsurface materials seems likely to be very limited and may be of questionable environmental significance. Nevertheless, in view of the current state of knowledge, sorption should not be ignored in efforts to remove such compounds from contaminated aquifers. Perhaps the most important sorption questions in regard to strategies for aquifer remediation pertain to sorption kinetics in low carbon aquifer systems. The gradual approach to sorption equilibrium observed in this work, as well as in recent studies by others (References 52, 53), suggests time-dependent release during contaminant desorption. This has important implications in modeling pollutant transport and in aquifer remediation.

## SECTION IV

### CONCLUSIONS

The information gained from this research should be significant in developing efficient, cost-effective strategies for decontamination of ground waters polluted by organic chemicals, including particularly chlorinated aliphatic hydrocarbon solvents and aromatic hydrocarbon constituents of distilled petroleum products.

This work clearly shows that soil microbial communities supported on gaseous aliphatic hydrocarbons can biodegrade TCE and related compounds under aerobic conditions. Apparently, this is the result of cometabolism of the halogenated compounds by those microorganisms present in the soil which use the gaseous hydrocarbons as primary substrate for oxidative metabolism. This discovery is especially important since it enhances the possibility of using biodegradation-based strategies to solve ground water pollution problems involving chlorinated organic solvents. Although these substances can be biotransformed under anaerobic conditions, complete degradation is not likely to be achieved, resulting in the accumulation of undesirable intermediates such as vinyl chloride which may be more hazardous, more mobile, and more difficult to remove from the water by conventional treatment methods. The aerobic cometabolic biodegradation process described in this research appears to result in relatively complete mineralization of halogenated alkyl hydrocarbons, without production of persistent intermediates. Hence, it possesses high potential as the basis for methodologies for removal of chlorinated hydrocarbon solvents from polluted ground water, both in situ and in surface-based treatment systems.

The potential of this microbial process as the basis for surface-based systems for ground water renovation is reiterated by the laboratory-scale fixed film bioreactor studies conducted as part of this research program. These studies, in conjunction with the basic process work, indicate strongly that field-scale fixed film bioreactors using gaseous aliphatic hydrocarbons as primary substrate should be quite effective for onsite renovation of ground water pumped from aquifers contaminated with TCE. This biological methodology appears especially attractive because of its probable low cost as predicted by preliminary economic analysis and its advantage over air stripping and carbon adsorption in terms of pollutant destruction. However, the failure to achieve removal of 1,1,1-trichloroethane in the laboratory-scale bioreactor experiments, coupled with inconsistencies in rates and extents of degradation of the various chlorinated aliphatic compounds observed in basic process studies, emphasizes the need for better understanding the factors controlling pollutant degradation and bioreactor operating characteristics.

Because of the high promise of fixed-film bioreactor methodology for renovating ground water contaminated by TCE and related substances, pilot-scale studies of this methodology should be initiated as soon as possible. It is imperative, however, that this work be done in conjunction with additional laboratory fixed film bioreactor studies designed to better

define the effects on pollutant removal of bioreactor operating and design parameters such as type and concentration of primary substrate and nature and concentration of pollutants. In addition, further fundamental research to better elucidate the aerobic cometabolic degradation of chlorinated aliphatic hydrocarbons is needed to provide an improved basis for both surface bioreactor and in-situ methodologies for renovation of ground water polluted by these substances.

The relatively rapid and extensive biodegradation of benzene and several alkylbenzenes in anoxic aquifer materials observed during this research was surprising, since these compounds have generally been considered recalcitrant to biotransformation in anaerobic environments. Anaerobic biotransformation of low molecular weight hydrocarbons in subsurface environments has significant implications in addressing ground water pollution problems involving distilled petroleum products. Because of the relatively high water solubility of the aromatic constituents of petroleum distillates, releases of gasoline and other light hydrocarbon fractions into the subsurface often produce plumes of polluted ground water containing benzene and alkylbenzenes in solution at individual concentrations of 10-100 mg·L<sup>-1</sup>. Approximately 20-200 mg·L<sup>-1</sup> of oxygen would be required for complete aerobic degradation of such concentrations of hydrocarbons. Because pristine ground water commonly contains 5 mg·L<sup>-1</sup> of oxygen, a plume of this intensity would have to admix with 40 equivalent volumes of pristine water before the plume could be renovated. However, if anaerobic biodegradation of the aromatic pollutants also occurred within the plume, the oxygen demand would be reduced and migration of the contaminants would be decreased. Hence, it is important to consider anaerobic biodegradation of the aromatic hydrocarbons in assessing the probable impact on ground water quality of releases of petroleum distillate products into the subsurface as a basis for selecting appropriate remedial action. Otherwise, levels of remediation that are excessive and unnecessarily expensive are likely to be selected. Indeed, expensive remedial actions may be initiated in situations where natural biodegradation would prevent the contaminant plume from migrating to points of ground water withdrawal or discharge, and the only action necessary if anaerobic biotransformation were taken into account would be monitoring to ensure that migration greater than predicted did not occur.

Anaerobic biotransformation of aromatic hydrocarbons may also offer attractive possibilities as the basis for developing improved methodologies for bioremediation of aquifers contaminated by petroleum distillates. If such biodegradation can occur as rapidly and extensively as indicated by these studies, then it may be possible to enhance this process in anoxic aquifers to achieve high levels of in-situ decontamination. It is of particular interest to note that electron receptors for anaerobic metabolism such as nitrate, sulfate, and bicarbonate are usually much more available in subsurface environments than molecular oxygen and, hence, not nearly so likely to become limiting in respect to pollutant biotransformation in such environments. Also, because these electron receptors are much more water-soluble than oxygen, replenishment of depleted concentrations of these substances in subsurface environments should be much more readily accomplished than restoration of oxygen concentrations to needed levels.

The ability to account for anaerobic biodegradation of aromatic hydrocarbons in predicting the impact on ground water quality of releases of petroleum distillates into the subsurface, as well as the development of methodologies based on anaerobic biodegradation for renovation of ground water contaminated by aromatic hydrocarbons, are dependent on further definition of the biotransformation process involved. Hence, it is recommended that research to more clearly describe the biodegradation of low molecular weight aromatic hydrocarbons in anoxic subsurface environments be undertaken. In particular, this work should elucidate the biotransformation process, including the microbes involved, the pathways of degradation including intermediates produced, the electron receptors involved, and other requisites for metabolism.

The sorption studies conducted as part of this research developed considerable data supporting the supposition that components other than the native organic carbon of low-carbon aquifer materials can exert a significant influence on the sorption of organic pollutants. The investigations involving benzene, dichlorobenzene, trichloroethylene, and perchloroethylene were especially illustrative. A substantial portion of the observed sorption of these compounds on various aquifer materials containing less than approximately 0.2 percent TOC could not be attributed to hydrophobic partitioning to the solid phase carbon. Overall, five aromatic compounds and two chlorinated alkenes ranging between 2.1 and 4.3 in octanol-water partition coefficients were utilized in this work. All appeared to be sorbed onto low-carbon aquifer solids obtained from both above and below the water table to a greater extent than would be predicted based on carbon-controlled hydrophobic sorption.

No significant correlations between the sorption of the various pollutants and those properties of the aquifer solids that are characteristic of the mineral components, such as clay content and total surface area, were indicated by the data obtained in these studies. Nevertheless, there is little doubt that the portion of the observed sorption that could not be attributed to the native organic carbon of the aquifer materials resulted from interactions of the organic pollutants with the mineral surfaces of these solids. It seems probable that, although the aquifer materials used in these studies were relatively well characterized, more extensive information on their composition, particularly in regard to clay content and mineralogy, was needed to elucidate the partitioning mechanisms involved in contaminant sorption by these low-carbon solids. Consequently, additional research employing low-carbon aquifer materials which are characterized in even greater detail, especially in regard to the mineral components, appears necessary if parameters which may be employed to more accurately predict sorption of organic pollutants in low-carbon subsurface environments are to be identified.

Estimates of the sorption of low to intermediate polarity organic pollutants by low-carbon aquifer materials based only on the organic carbon content of these materials are likely to be too low because of the contribution of pollutant-mineral surface interactions to the overall sorption process. For compounds such as benzene and trichloroethylene, for which total sorption on low-carbon aquifer solids is likely to be quite low, the error in predicting contaminant movement which results



from failure to consider the mineral component of sorption may be insignificant in relation to errors introduced by uncertainties in other parameters used in such predictions, such as field-measured water velocities. For other pollutants, however, omission of the mineral component of sorption may lead to significant over-estimation of pollutant mobility and, conversely, low estimates of the time required to achieve removal of pollutants from a contaminated aquifer. Until the variables which govern pollutant sorption onto aquifer materials containing very low levels of native organic carbon are better defined, it will probably be necessary to conduct site-specific sorption experiments utilizing the relevant aquifer material and pollutants when attempting to develop an optimized strategy for decontamination of a polluted aquifer and to predict the duration and economics of proposed remedial activities.

The data obtained during these studies clearly show that methods commonly used for sorption studies, which determine quantities sorbed by measuring differences in solution phase concentrations of sorbate, have serious inadequacies for determining the sorption of compounds of low to moderate hydrophobicity on subsurface solids of low sorptive capacity. For such compounds and sorbents, sorption is best determined by extracting and measuring the quantity of compound actually sorbed on the solid phase rather than measuring solution phase concentration differences. The procedure based on sorbent extraction which was developed and employed in this work provides a much more precise determination of sorption coefficients, especially if solids solution ratios are kept low to minimize errors caused by colloidal sorbents which may be contributed to the solution phase by the solids.

The gradual approach to sorption equilibrium observed in these studies, as well as in recent work by others, suggests time-dependent release during pollutant desorption. This phenomenon has major implications for development of effective strategies for decontamination of polluted aquifers and should be investigated further.

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